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JANUARY 1960
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The Dispersion of Wool Protein by Thiols in Acid Solution

W. E. Savige

Division of Protein Chemistry (formerly Biochemistry Unit), C.S.I.R.O. Wool Research Laboratories, Parkville, N.2, (Melbourne), Victoria, Australia

Abstract

Wool suffers a loss in weight of up to 50% in 24 hr. on treatment at 50–60° C. with a salt-free aqueous solution of a particular thiol containing sufficient selected acid to bring the pH value to approximately 2. The extent of extraction depends on a number of factors such as temperature, time, pH, and the nature or concentration of thiol, acid, and any salt or other reagent which may be present. The dispersed keratin appears to undergo no appreciable chemical degradation apart from reductive fission of the disulfide bonds of the cystine residues.

Apart from a small amount of residue consisting of cell membranes, wool is completely solubilized by treatment with concentrated aqueous thioglycollic acid at 60° C. in the absence of salts.

Introduction

Certain thiols such as thioglycollic (mercaptoacetic) acid and mercaptoethanol can dissolve keratins in aqueous solution at pH values above 10 [8, 9, 12]. They are less effective as dispersing agents at pH values between 7 and 10 unless hydrogen bond-breaking reagents are present [9, 12]. Until the present time wool was believed to be insoluble in aqueous acid solutions of thiols [9, 17], the disulfide bonds of the cystine residues being not so extensively reduced as in alkaline solution [7, 17].

The present investigations followed the observation that, when using the procedure of Leach [13] for hydrolyzing wool with boiling dilute acids, thioglycollic acid caused more rapid dissolution of the wool than did either hydrochloric or oxalic acid. In subsequent experiments wool was found to be soluble in aqueous thioglycollic acid under conditions of temperature and concentration at which little peptide hydrolysis would be expected to occur. In this paper it is shown that acid solutions containing thiols can in fact dissolve wool proteins, provided, among other things, that salts are absent or present only in very low concentration.

Experimental

Materials

Wool. Unless otherwise stated the wool used was Merino 64's which had been solvent scoured with the petroleum fraction "white spirit," washed with water, manufactured into a slubbing, and further purified in the laboratory by washing in cold light petroleum, ethanol, and finally distilled water. It was conditioned at 70% relative humidity and 20° C. and the moisture content determined by drying a sample to constant weight at 105° C., thus en-

abling ready calculation of "dry weight" of all samples weighed out. The mohair, human hair, and Lincoln wool were purified similarly.

Reagents. Commercial thioglycollic acid (E. P. Keogh, Melbourne) and mercaptoethanol (L. Light, England) were used; most of the other thiols were prepared by Dr. J. M. Swan and Mr. I. W. Stapleton of this laboratory. The concentrations of thiol solutions were determined by titration with 0.1 *N* iodine. Most of the acids were from British Drug House Ltd. Solutions of some acids were prepared by passing aqueous solutions of the salts, for example ammonium thiocyanate, through a column of the ion exchange resin Zeokarb 225 and eluting with water.

Methods

Estimation of solubility. A sample of wool (about 0.2 g.) was treated with 20 ml. of the appropriate reagents in a stoppered glass or polyethylene tube and heated without agitation in a constant temperature bath, usually at 50° C. or 60° C. ± 0.1° C. for 24 hr. When a volatile reagent was present special "Quickfit" tubes with spring-loaded stoppers were used. If a low concentration of thiol were used, the air in the tube was displaced with nitrogen, but in most experiments where a large excess of thiol was employed this precaution was found to be unnecessary. The residue after digestion was usually collected on a disc of No. 4 Whatman filter paper in a Buchner funnel (the filtrate being retained if required for pH determination) and washed with a large volume

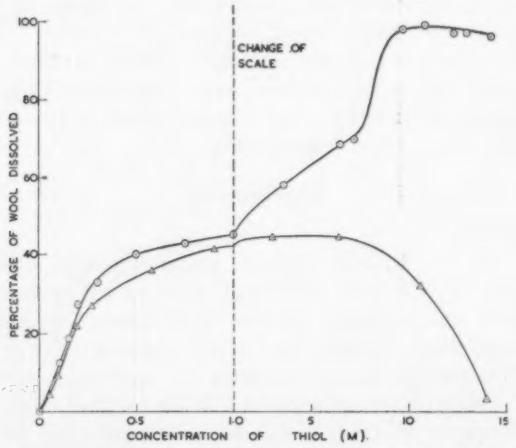

Fig. 1. Effect of concentration of thiols on solubility of wool in aqueous acid solution, 60° C., 24 hr.; ⊙ = thioglycollic acid and ◬ = mercaptoethanol in 0.5 *M* acetic acid.

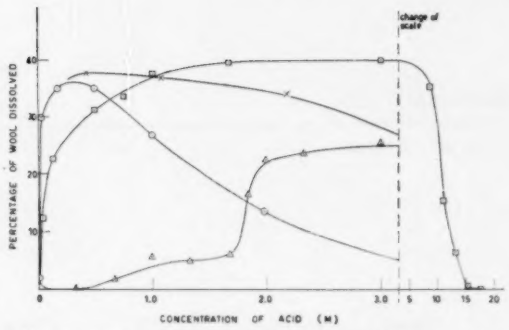

Fig. 2. Effect of concentration of weakly dissociated acids on solubility of wool in 0.4 *M* aqueous mercaptoethanol, 60° C., 24 hr.; ⊡ = acetic acid, × = formic acid, ⊙ = citric acid, and ◬ = boric acid.

of water initially without suction for 30 min., then with suction. If the reagent used included a water-insoluble component, the residue was finally washed with ethanol. The residue was then detached from the filter paper and dried to constant weight at 105° C. If the residue became disintegrated it was collected on a filter paper of known dry weight and both paper and residue dried and weighed. All results are expressed as percentage of wool dissolved on a dry weight basis. For an experiment in which it was desired to recover the soluble proteins, the combined filtrate and washings were concentrated to a thin syrup in a rotary evaporator, then the proteins precipitated by addition of ethyl acetate.

Estimation of thiol and disulfide groups. Samples weighing 0.14 g. were hydrolyzed by heating with 8.3 ml. 6 *N* HCl at 105° C. for 24 hr. in a sealed tube, after which the thiol and disulfide contents were determined essentially according to Shinohara [20], except that the color values were calibrated with a standard solution of pure cystine in 1 *N* HCl.

Detection of lanthionine. Aliquots (0.2 ml.) of the above hydrolysate were spotted on a polythene sheet and dried in a vacuum over NaOH and H_2SO_4. The presence of lanthionine in the residues was determined essentially according to Thompson [28]. A one-phase solvent mixture of 4 parts mesityl oxide, 1.2 parts 90% formic acid, and 1 part water was preferred to the two-phase system generally used [1, 28], as it was less wasteful of solvent and gave the same R_f values as those reported by Thompson for cystine, lanthionine, cysteic acid, lanthionine S,-S-dioxide, and lysine.

Detection of aspartic acid. In selected experiments the filtrate obtained from the partly dissolved

wool was concentrated by means of a rotary evaporator and chromatographed on filter paper using 75% aqueous phenol as solvent to reveal any aspartic acid present.

Estimation of free amino groups. Samples weighing 2 mg. were treated with 1 ml. of 0.1 *M* potassium iodoacetate at pH 8; then the free amino groups were determined by the ninhydrin method of Harding and MacLean [10] as modified by McPhee [16].

Results

Extraction with Thioglycollic Acid

The extent of dissolution of wool occurring during 24 hr. at 60° C. increased markedly with increasing concentration of thioglycollic acid (Figure 1), reaching 40% at an acid concentration of 0.5 *M* when the pH value was 2.0. With further increase in concentration the extent of extraction continued to increase, the wool being almost completely dissolved at thiol concentrations greater than 9 *M*. In parallel experiments using formic acid, which is of comparable strength to thioglycollic acid, no extraction was observed up to 14 *M* (65%) acid concentration, and the wool appeared to be undamaged. An aqueous solution of a neutral thiol such as mercaptoethanol, when used alone, was found to extract less than 3% of wool protein.

Extraction with Mercaptoethanol in Aqueous Acetic Acid

The extent of extraction of wool with mercaptoethanol in the presence of 0.5 *M* acetic acid (pH 2.6) increased up to a thiol concentration of 1.5 *M*, when 45% of the wool protein dissolved (Figure 1). The 1.5 *M* concentration represents a 150-fold excess of mercaptoethanol sulfhydryl groups over half-cystine residues in the 0.2-g. sample of wool. Increasing the mercaptoethanol concentration to 9 *M* (65%) had no further effect, and beyond this concentration the amount of wool extracted decreased.

When the concentration of acetic acid was varied in the presence of 0.4 *M* mercaptoethanol, the extraction reached a maximum of 40% at an acid concentration of 2–3 *M* (pH 1.9–2.3), gradually decreased with further increase in acid concentration to 10 *M* (pH *ca.* 1.5), and then fell off rapidly (Figure 2). The optimal concentrations of mercaptoethanol and acetic acid, 3.0 *M* and 2.5 *M* respectively, removed 47% of the protein from wool during 24 hr. at 60° C.

TABLE I. Solubility of Wool in 0.5 *M* Solutions of Various Thiols in 2 *M* Acetic Acid

Thiol used	Extraction conditions* 60° C., 24 hr. Wt. loss, %	50° C., 64 hr. Wt. loss, %
Mercaptoethanol	41	
Thioglycollic acid	41	37
Mercaptosuccinic acid	41	34
Cysteine	40	
Acetylcysteine		29
β-Mercaptoisobutyric acid	37	
Thiophenol	37	
β-Mercaptoethyl ether (0.25 *M*)	35	
Ethyl thioglycollate		26
Benzyl mercaptan	26	
Mercaptoethylamine	11	
Isobutyl mercaptan	10	
Hydrogen sulfide (saturated)	8	
Thiolbenzoic acid		−9 (wt. gain)

* Liquor ratio was 1 : 100 for all experiments described in this paper.

Extraction Using Selected Thiols in Aqueous Acetic Acid

A number of selected thiols were compared at 0.5 *M* for their ability to extract wool in the presence of 2 *M* acetic acid. A high concentration of acid was employed to minimize variation in pH. Cysteine, acetylcysteine, thiophenol, and simple aliphatic sulfhydryl acids were found to be about equal in effect to mercaptoethanol when compared at 50–60° C. (Table I). Benzyl mercaptan was only moderately effective, while β-mercaptoethylamine, hydrogen sulfide, and the lower aliphatic mercaptans were even less effective.

Extraction Using Selected Acids in Aqueous Mercaptoethanol

A similar comparison was made of a series of acids in a solution containing 0.4 *M* mercaptoethanol. When comparisons were made at equal concentrations of the various acids, the results were difficult to interpret. When compared at various concentrations, the extent of extraction was found to vary with the particular acid employed (Figures 2, 3, and 4) and appeared to be related to the pH value. When the loss in weight was plotted against the pH of solutions containing hydrochloric, phosphoric, acetic, and boric acids—acids which vary widely in

the degree of dissociation—appreciable extraction was found to occur between pH 1 and 3, with a maximum about 2.1 (Figure 5). The extraction observed in HCl solutions exceeding 0.5 *N* in concentration occurred also in the absence of thiols and was ascribed to hydrolysis. Phosphoric acid at concentrations exceeding 5 *M* was similarly effective, but it produced a thick sludge, presumably of degraded protein.

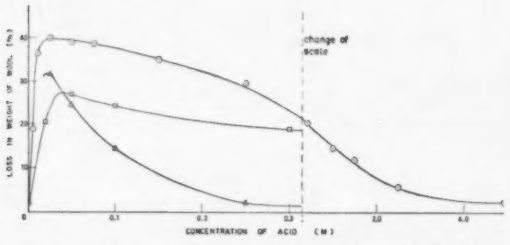

Fig. 3. Effect of concentration of moderately dissociated acids on solubility of wool in 0.4 *M* aqueous mercaptoethanol, 60° C., 24 hr.; ⊙ = phosphoric acid, △ = oxalic acid, and ⊡ =chloroacetic acid.

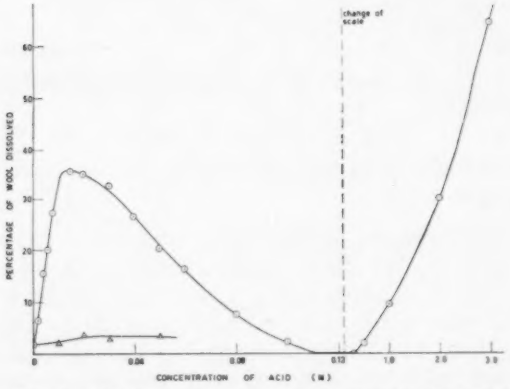

Fig. 4. Effect of concentration of strongly dissociated acids on solubility of wool in 0.4 *M* aqueous mercaptoethanol, 60° C., 24 hr.; ⊙ = hydrochloric acid and △ = sulfuric acid.

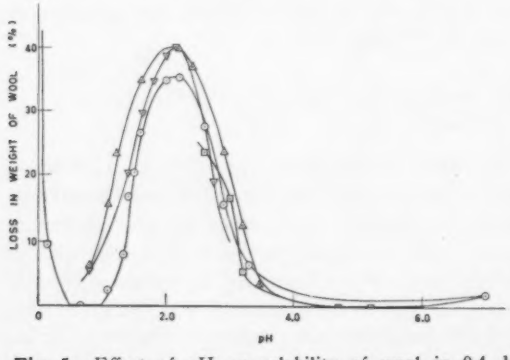

Fig. 5. Effect of pH on solubility of wool in 0.4 *M* aqueous mercaptoethanol, 60° C., 24 hr. in the absence of salts, the pH being controlled by varying the concentration of acid; ⊙ = hydrochloric acid, ▽ = phosphoric acid, △ = acetic acid, and ⊡ = boric acid.

The amount of extraction at pH *ca.* 2 in the presence of 0.4 *M* mercaptoethanol varied widely with some acids used (Figures 2, 3, and 4), the loss in 24 hr. at 60° C. for phosphoric, chloroacetic, dichloroacetic, and sulfuric acids being 40%, 27%, 13%, and 3% respectively. This phenomenon was studied further, using a much larger range of acids. Slight elevation of the pH during extraction due to adsorption of acid on the wool may have occurred in some instances, but the addition of buffer salts to the thiol solutions was precluded by the repressive effect of salts on the extractability. In some cases error may have been caused during measurement of the pH by partial precipitation of acid as the solution cooled. For these reasons the reported order of effectiveness of the different acids (Table II) may not be entirely correct. In the case of experiments carried out at pH 2.1 ± 0.2 the measured loss in weight of wool is believed to lie within 2% of the maximum loss obtainable with a particular acid under the standard experimental conditions. For experiments such as those with boric, aspartic, glutamic, and gallic acids which, due to low solubility or low dissociation constant of the acid employed, were carried out at pH values appreciably higher than 2, the measured loss in weight of wool was almost certainly lower than it would have been if a pH of 2.1 had been attainable.

Aliphatic carboxylic or sulfonic acids with no bulky hydrophobic side chains and the inorganic acids hydrofluoric, hydrochloric, hydrobromic, phosphoric, and phosphorous were very effective in extracting wool at pH *ca.* 2 in the presence of 0.4 *M* mercaptoethanol (Table II), 30–40% of wool protein being dissolved in 24 hr. at 60° C. Organic acids containing unsaturated groups or hydrophobic side chains such as halogen atoms or benzene rings were less effective (5–30% protein dissolved), as were also the inorganic acids boric and hydriodic. Still others such as pyruvic acid, aromatic carboxylic or sulfonic acids, and the inorganic sulfuric, sulfurous, perchloric, and thiocyanic acids either caused no appreciable loss in weight ($< 5\%$) of the wool or actually increased the weight, due presumably to adsorption.

In the case of organic acids with hydrophilic side

chains, the size of the side chain did not appear to affect appreciably the extent of dissolution of reduced wool protein, as evidenced by the results for gluconic acid (36%) and hydroxyethanesulfonic acid (38%), nor did the nature of the acidic function—*cf.* for example, acetic (40%), ascorbic (40%), and methanesulfonic (35%) acids. However the size of hydrophobic side chains was important, as evidenced by the difference in effectiveness among methanesulfonic (35%), ethanesulfonic (20%), and *p*-toluenesulfonic (− 11%) acids, and also among acetic (40%), chloroacetic (27%), dichloroacetic (13%), trichloroacetic (− 6%), and trifluoroacetic (26%) acids. For inorganic acids, the order of effectiveness appeared to be $H_3PO_4 = H_3PO_3 > HCl = HF > HBr > H_3BO_3 > HI = H_4P_2O_7 > H_2SO_4 = HCNS = HClO_4 = H_2SO_3$, although boric and sulfurous acids may be out of place, as the experiments were carried out in these cases at pH values of 2.6 and 2.8 respectively.

In the case of wool which had been treated at 60° C. for 24 hr. with 0.015 *M* perchloric acid in the presence of 0.4 *M* mercaptoethanol and had lost 4.6% in weight, it was found that the amount of disulfide reduction (36%) was virtually the same as for wool treated with a much lower concentration (0.002 *M*) of HCl in the presence of the same concentration of mercaptoethanol (wt. loss 6.5%, disulfide reduction 29%).

Effect of Additives

Determinations were made of the loss in weight of wool samples on being heated at 50° C. for 64 hr. in 0.45 *M* mercaptoethanol in the presence of various concentrations of ionizable ammonium, the pH being adjusted to 2.1 in each experiment by addition of the required amount of phosphoric acid. It was found (Figure 6) that a solution containing 0.1 *M* ammonium and 0.25 *M* phosphate extracted much less wool protein than solutions not containing

TABLE II. Solubility of Wool in 0.4 *M* Mercaptoethanol Containing Selected Acids at pH *ca.* 2*

Acid	Concentration of acid, *M*	Final pH	Loss in weight, %
Strong Acids			
Hydroxyethanesulfonic	0.02	2.1	38
Hydrochloric	0.02	2.0	35
Methanesulfonic	0.016	2.1	35
Hydrobromic	0.02	2.2	30
Trifluoroacetic	0.02	2.2	26
2-Methylpropanesulfonic	0.02	2.1	24
Ethanesulfonic	0.016	2.1	20
Hydriodic	0.02	1.8	13
Pyrophosphoric	0.02	2.2	13
β-Mercaptoethanesulfonic	0.02	2.0	12
Perchloric	0.015	2.2	5
Sulfuric	0.01	2.1	3
Thiocyanic	0.02	1.8	2
Trichloroacetic	0.02	2.0	− 6
Sulfosalicylic	0.015	2.2	− 7
p-Toluenesulfonic	0.025	1.8	−11
Dodecylsulfuric	0.03	2.6	−24
Moderately Strong Acids			
Cysteic	0.05	2.0	44
Phosphoric	0.025	2.2	40
Phosphorous	0.02	2.2	38
Hydrofluoric	0.1	*ca.* 2.0	34
Oxalic	0.025	2.0	32
Saccharic	0.08	2.5	32
Chloroacetic	0.05	2.1	27
α-Chloropropionic	0.1	2.0	25
Dichloroacetic	0.02	2.2	13
Maleic	0.1	2.3	8
Fumaric	0.1	2.3	2
Sulfurous	0.1	2.8	0
Pyruvic	0.1	2.3	− 3
Salicylic	0.1	2.4	− 5
Phthalic	0.1	2.2	− 7
Weak Acids			
Succinic	1.0	2.2	41
Acetic	3.0	2.1	40
Ascorbic	1.0	2.4	40
Tartaric	0.25	1.9	38
Formic	0.44	2.0	37
Lactic	1.1	1.8	37
Citric	3.3	1.8	36
Propionic	2.5	2.4	36
Malic	0.5	2.0	36
Gluconic	1.0	2.1	36
Malonic	0.2	2.0	35
Butyric	2.5	2.5	34
Glycolic	1.0	2.0	34
Diglycolic	0.37	1.9	33
Isobutyric	2.5	2.6	32
Gallic	0.5	2.8	28
Aspartic	0.2	3.0	28
Boric	3.0	2.6	25
Isovaleric	2.5	2.7	24
Sulfanilic	0.25	2.1	23
Glutamic	0.2	3.4	21
Crotonic	1.0	2.6	15
Furoic	0.18	2.0	12
Taurine	1.5	4.2	4
Benzoic	0.2	3.0	3

* All solutions were salt-free, and the wool was heated at 60° C. for 24 hr.

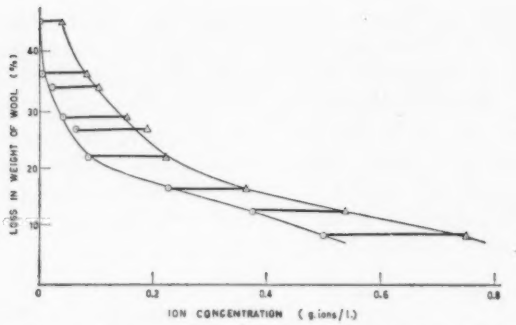

Fig. 6. Combined effect of ammonium (⊙) and phosphate (△) total ion concentrations giving a pH of 2.1 ± 0.1 in 0.45 *M* aqueous mercaptoethanol, 50° C., 64 hr.

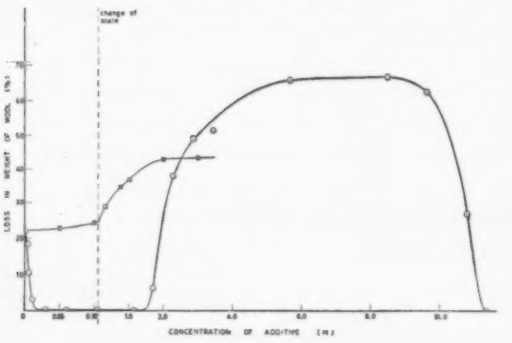

Fig. 7. Effect of concentration of additives on solubility of wool in 0.5 *M* thioglycollic acid, 50° C., 24 hr.; ⊡ = thiourea and ⊙ = phenol.

ammonium—whether compared with a parallel experiment at the same pH but at a different phosphate concentration (0.07 *M*) or with an experiment at the same phosphate concentration but at a different pH (1.7). Extraction of wool protein was reduced similarly by sodium ions and also to a lesser extent by the nonionic detergent "Lissapol NX" (octyl cresyl polyoxyethylene); the cationic detergent myristylamine appeared to assist dispersion slightly.

The dispersion of wool proteins in acid solutions of thiols was increased by the presence of hydrogen bond-breaking reagents despite the accompanying slight rise in pH. In the presence of 2 *M* thioglycollic acid (Table III) or of a solution containing 2 *M* mercaptoethanol and 2 *M* acetic acid, thiourea was found to be the most effective of the reagents employed. In the case of urea, some decomposition occurred, leading to a marked rise in pH. Formamide and methylformamide (2 *M*) had an inhibitory effect. The effect of varying the concentration of thiourea in the presence of 0.5 *M* thioglycollic acid

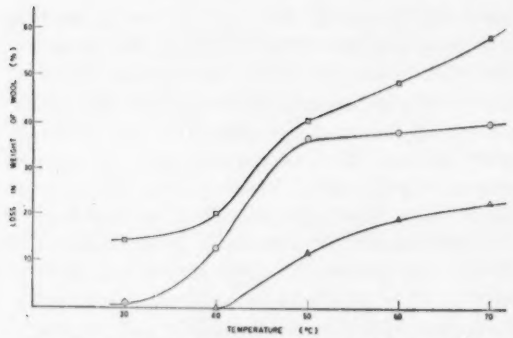

Fig. 8. Effect of temperature on solubility of wool in aqueous acid solutions of thiols; ⊡ = 2 *M* thioglycollic acid, ⊙ = 0.4 *M* mercaptoethanol in 2 *M* acetic acid, and △ = 0.4 *M* mercaptoethanol in 2 *M* boric acid.

(Figure 7) is in marked contrast to the results using phenol. With thiourea, extraction increased with concentration, reaching a maximum at 2 *M*. With phenol, dispersion was markedly inhibited at concentrations below 1.5 *M* and also at very high concentrations, but at phenol concentrations from 3 to 10 *M*, where a two-phase system existed, dissolution was greatly assisted.

Effect of Temperature and Time

Extraction of wool by mercaptoethanol in the presence of acetic acid was not extensive at low temperatures (Figure 8), but showed a 3-fold increase between 40 and 50° C., a further rise in temperature having a comparatively slight effect. In the case of stronger acids with mercaptoethanol, or 2 *M* thioglycollic acid alone, there was no such flattening in the curve.

Extraction of wool by 0.5 *M* thioglycollic acid at 50° C. appeared to proceed in two stages, the first of which was virtually complete in 2 days with $\frac{1}{3}$ of the wool dissolved, and the second still incomplete in 3 weeks with $\frac{1}{2}$ of the wool protein dispersed. In the presence of thiourea, similar results were obtained, the first stage being complete in only 12 hr., but, after 4 days, dispersion was still less than 60%.

Properties of the Wool Residues and Extracted Proteins

After extraction of wool with thiols under acid conditions, the properties of the residues varied considerably according to the conditions of the treatment. For example, wool treated with 0.5 *M* thioglycollic acid at 50° C. for 2 days gave a residue

which superficially resembled the original wool, yet 30% of the wool protein had been extracted. The scale pattern was still in evidence, although the fibers were somewhat swollen and considerably weakened. An electron micrograph of a cross section of a fiber remaining after such treatment, studied by Rogers [18], showed up markedly the bilateral structure. The appearance of fibers through the polarizing microscope was similar to that described by Fraser and Rogers [6] for wool extracted with alkaline thioglycollate, indicating preferential swelling of one segment. However, comparative experiments on other keratin fibers (Table IV) such as mohair (ortho type) and human hair and mutant Merino wool (para types) indicated that no simple conclusion could as yet be drawn with regard to preferential extraction.

The solubility of Merino wool in aqueous thioglycollic acid was decreased to less than half the original value when previously heated in water at 100° C. for 24 hr.

The residue obtained after extracting wool with aqueous thioglycollic acid at 60° C. usually commenced to disintegrate when approximately half of the wool protein had been extracted. The small residue (1–2%) remaining from the action of thioglycollic acid at higher concentrations or temperatures appeared to consist of cell membranes. The residues from treatment of wool with mercaptoethanol were usually considerably swollen, particularly when the acids employed were organic acids or phosphoric acid. The protein solutions became turbid on dialyzing against distilled water, while a precipitate was formed on adding sodium chloride or on bringing the pH of the liquor to *ca.* 5 by the addition of ammonia. Addition of aqueous sodium hydroxide caused the appearance of a precipitate, which soon redissolved on further addition of alkali.

An attempt was made to measure the extent of reduction both in the wool residues and in the recovered protein, the method of Shinohara [20] being used. These results, although not always consistent, indicated that in a typical experiment (for example, treatment of wool with 0.5 *M* thioglycollic acid at 50° C. for 3 days, initial pH 2.0) the wool residue and the dissolved protein were reduced to virtually the same extent, approximately 70–90% of the "disulfide plus sulfhydryl" sulfur present being in the reduced state. However, the total disulfide plus sulfhydryl sulfur in both wool residue (*ca.* 800–980 μg.-atom/g.) and dissolved protein (*ca.* 250 μg.-atom/g.) was significantly less than for the original wool (984 μg.-atom/g.).

A series of experiments was carried out in which 0.2-g. samples of wool were heated for 24 hr. in 20 ml. phosphate buffer solution over the pH range 2.0–4.5. The presence of lanthionine was readily detected in the wool which had been heated at 100° C. at pH 4.0 or 4.5, but traces only were detected in wool heated at pH 2.0–3.5; no lanthionine was detected in wool heated at 60° C. at pH 2.0 or 4.5. In none of these experiments did the wool suffer any loss in weight except in the treatment at pH 2.0 for 24 hr., when a loss of 4% occurred. In every experiment the loss in cystine, as estimated by the method of Shinohara, was small, the greatest loss being 4.5% at pH 4.5 for 24 hr. Further experiments, carried out in the presence of sodium or ammonium chloride in order to prevent dissolution of the wool, showed that lanthionine formation was catalyzed by the presence of a thiol such as 0.5 *M* mercaptoethanol or thioglycollic acid at 50 or 60° C. at pH 2.0–4.0, but again to less than 5% of the theoretically possible amount in 24 hr.

TABLE III. Solubility of Wool in 2 *M* Thioglycollic Acid Containing Various Additives*

Additive (2 *M*)	Wool dissolved, %
Thiourea	35
Urea	32
Resorcinol	30
Phenol	29
Urethane	27
Methylacetamide	26
Acetamide	23
Nil	17
Methylformamide	10
Formamide	2

* The wool was heated at 60° C. for 24 hr.

TABLE IV. Solubility of Various Keratins in 0.5 *M* Thioglycollic Acid*

Fiber	Wool dissolved, %
Mutant Merino wool	52
Mohair	47
Steely Merino wool	42
Normal Merino 64's wool	37
Lincoln wool	34
Human hair	29

* The wool was heated at 50° C. for 3 days.

Free amino acids such as aspartic acid and glycine could not be detected in the filtrates obtained from treatment of wool at 60° C. for 24 hr. with 0.5 *M* thioglycollic acid. Free amino groups in the wool residue amounted to 250 μg.-atom N/g., in the recovered protein 230 μg.-atom N/g., and in the original wool 215 μg.-atom N/g.

Discussion

The results show that up to 50% of the proteins comprising wool are readily extracted on treatment of the fiber at 50–60° C. with an aqueous solution of a particular thiol in the presence of a selected acid in precise concentration to give the solution a pH of approximately 2. Any proposed explanation must take into account the similar but more rapid extraction of wool by thiols occurring at pH values above 10 [8, 9] and the normally low solubility in thiol solutions not containing hydrogen bond-breaking reagents at pH 1 and within the range 3–10. It is likely that the wool is first converted into discrete protein molecules following fission of disulfide bonds of the cystine residues, salt links, and hydrogen bonds. The solubility of the reduced protein would then be dependent among other things on its over-all net charge. Harris et al. [7, 17] have shown that reduction of wool by 0.2 *M* thioglycollic acid occurs to the extent of approximately half of the cystine residues in 20 hr. at 35° C. at pH values between 2 and 6, then increases markedly at higher pH. Salt links would be expected to be fissionable at pH 2 or 10, but not in the neutral range. Fission of hydrogen bonds, accompanied by swelling, is brought about to a certain extent by the water present, and can be assisted by other agents such as urea, thiourea, phenol, or weak organic acids. The observation that hydrogen bond-breaking reagents facilitate the extraction of wool proteins by thiols in acid solution is in line with the known effect in neutral and alkaline solutions [12, 29], although the order of effectiveness of the reagents is not necessarily the same in each case (*cf.* Table III and [12]). The over-all net charge on a protein molecule depends on pH and the nature and concentration of extraneous ions, anion adsorption being high at very low pH. It is of interest that the swelling of collagen is maximal at pH 2 [15].

It is believed that with proper choice of conditions the reduced wool proteins can be extracted by the acid-thiol method without significant degradation such as lanthionine formation, hydrolysis, or deamidation. It is well established [5] that cystine residues in proteins are readily converted to lanthionine by treatment with certain alkaline reagents, but the only suggestion that this can occur under acid conditions is the claim by Houff, Wills, and Beaumont [11] that on treating wool for 24 hr. in boiling aqueous buffer at pH 6.7 or 4.5, 25–40% of the cystine is lost and a considerable quantity (*ca.* 75% of the theoretical) of lanthionine is formed. However, the present work has shown that less than 5% of the cystine residues are converted to lanthionine under conditions employed in the acid-thiol method. Also, no free amino acids were detected in the filtrates, nor was there any undue increase in the number of free amino groups in either the wool residues or the recovered proteins, this result being expected as extraction is carried out under conditions milder than those required for partial hydrolysis or deamidation. For example, Steinhardt and Fugitt [23] have shown that no hydrolytic peptide fission occurs on heating wool with 0.05 *M* HCl at 65° C. for 24 hr. and only *ca.* 3.5% deamidation was observed. Thus under conditions likely to be employed with the acid-thiol method, for example using 0.04 *M* phosphoric acid or 3 *M* acetic acid at 50–60° C. in the presence of 1 *M* mercaptoethanol, hydrolysis or deamidation would not be expected to be significant, as the acids which are effective in causing deamidation are those such as dodecylsulfuric acid [23] having high anion affinities, and these are not likely to be used in the acid-thiol extraction method.

It is of interest that the reduced proteins obtained by alkaline thioglycollate extraction of wool are reported to be soluble in strongly acid solution [9]. With the acid method in the absence of a hydrogen bond-breaking reagent, no more than 50% of the wool can be readily extracted under suitably "safe" conditions. This incompleteness of dispersion may result from preferential extraction of certain components or, on the other hand, extraction may be accompanied by hydrothermal changes (denaturation) of the kind reported by Lennox [14]. The residue would then represent the denatured material. These changes may not be important in the present instance, as Swan [27] has shown that wool can be "denatured" insofar as its solubility in alkaline thioglycollate is concerned (e.g., by heating at 45–50° C. in 0.05 *M* potassium carbonate), but such wool is still soluble in thioglycollic acid at pH 2.

The order of effectiveness of thiols in dispersing wool protein at pH 2 (Table I) does not correspond with their relative effectiveness in reducing wool at pH 7.0 (0.5 *M*, 37° C.) as determined by Stapleton and Swan [26], who found benzyl mercaptan >> isobutyl mercaptan > thioglycollic acid, nor with their order in dissolving wool at pH 10.4—thioglycollic acid > isobutyl mercaptan = benzyl mercaptan >> cysteine > thiophenol [26]. The almost complete dissolution caused by high concentrations of thioglycollic acid at 60° C., even in the pH 1 region where conditions for extraction are normally unfavorable, contrasts with the smaller degree of dispersion (maximum recorded 47%) caused by high concentrations of mercaptoethanol in the presence of acetic acid.

At first glance the order of effectiveness of moderate to strong acids in assisting mercaptoethanol to dissolve wool proteins at pH 2 (Table II)—apart from the anomalous position of sulfuric acid—shows some resemblance with the order of the lyotropic series. However, the order of the lyotropic series is mainly concerned with adsorption effects at neutral pH, and the findings of Speakman and Stott [22] and of Steinhardt, Fugitt, and Harris [24] indicate that the order of adsorption in acid solution does not necessarily follow the lyotropic series. For example, sulfate ions, though more weakly adsorbed than chloride at pH 7, are much more strongly adsorbed than chloride at low pH values according to the order of anion affinity constants determined by Steinhardt et al.: phosphate (as $H_2PO_4^-$) > chloride > bromide > *p*-toluenesulfonate > trichloroacetate > pyrophosphate (as $H_2P_2O_7^=$) > sulfate (as $SO_4^=$) > sulfosalicylate > dodecylsulfate. The results of the present work therefore tend to show that in the presence of moderate to strong acids at pH 2, thiols disperse wool protein effectively if the acid used has a low anion affinity constant (for example HCl and H_3PO_4), but solubility is inhibited if the acid, as with perchloric [2] or dodecylsulfuric acid, has a high affinity constant and/or is known to be a specific protein precipitant. This, however, does not hold true for weak acids, which, although weakly adsorbed at pH 7, have been shown by Steinhardt, Fugitt, and Harris [25] to combine extensively with wool at low pH values—not as anions but as undissociated molecules. This form of adsorption apparently does not inhibit dissolution of the reduced proteins; in fact these weak acids, such as acetic acid, should assist dispersion by acting as hydrogen bond-breaking reagents. It would therefore appear that, for a given acid, dispersion is dependent not so much on the total amount of acid adsorbed as on the extent of each type of adsorption—as hydrogen ion, anion, and undissociated acid. Naturally there can be no clear-cut lines of demarcation among the three categories, as exemplified by chloroacetic acid, where all three types of adsorption would be expected to occur to a significant extent. With sulfuric and pyrophosphoric acids, significant adsorption should occur both of hydrogen ions and anions; also, these divalent ions would possibly tend to hold the reduced protein molecules together by ionic bonds and further reduce dispersion. Anion adsorption, then, is apparently the main factor inhibiting dissolution of the reduced wool proteins. The observation that wool was reduced by mercaptoethanol in the presence of $HClO_4$ to approximately the same extent as in the presence of HCl indicates that inhibition of dissolution brought about by an ostensibly highly adsorbed anion is not connected with the extent of reduction of the cystine residues. Anion adsorption, which results in the net positive charge on the protein being diminished, is reported by Crewther and Dowling [4] to occur at the interface between the protein and solution. This should tend to prevent the reduced proteins from diffusing into the solution. An alternative explanation is that the highly adsorbed anions bring about protein configurational changes.

For some weak acids also, dispersion is inhibited. The experiments carried out in the presence of ammonium and phosphate ions (Figure 6) appear to show that cations also inhibit dissolution, but this is difficult to demonstrate absolutely, as the anion concentration must also be changed in order to keep the pH constant.

Inhibition is apparently also caused by adsorption of phenol when present in low concentration, but at high concentration it assists dispersion, apparently by acting as a hydrogen bond-breaking reagent. This amplifies the observation by Speakman and coworkers [19, 21] that molar thioglycollic acid in phenol hydrate (equivalent to approximately 9 *M* aqueous phenol) dissolves wool.

The present finding that wool is solubilized by thiols at pH 2 may help towards a better understanding of diverse phenomena in wool chemistry—for example, the ability of certain insects to digest wool in the acid hindgut region of their alimentary tracts [30]. Also, it is probably a factor to be considered in explaining the depilatory action of dilute

organic acids on sheepskins, reported by Carrie, Moore, and Chisholm [3]. Such action would be expected if the prekeratin which contains a proportion of sulfhydryl groups is soluble at pH *ca.* 2 in the same manner as the reduced wool proteins described in the present work. If this explanation is correct, depilation would no doubt be assisted by carrying out the process at pH 2.1 in the absence of buffer salts. It is possible that the finding by Carrie et al. [3] that citric acid is a better depilatory than acetic acid may be due not so much to the nature of the acid but to the fact that their observations with the former acid were carried out at pH 2.1 to 2.42 and with the latter acid at pH 2.9 to 3.7.

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The Development of Washable Non-Iron Effects in Pure Wool Fabrics

A. J. Farnworth, M. Lipson, and J. R. McPhee

Division of Textile Industry, Wool Research Laboratories, Commonwealth Scientific and Industrial Research Organization, Geelong, Australia

Abstract

The use of reducing agents for setting wool has been extended to give washable non-iron effects on pure wool fabrics. Initially this was accomplished by applying the Si-Ro-Set process to garments made from shrinkproofed wool. This led to flat setting of fabrics in the mill by applying a dilute solution of a reducing agent to the fabric followed by immediate steaming on a blowing machine.

When preceded by shrinkproofing, this method of setting gives excellent washable non-iron effects on pure wool fabrics. Garments made from fabric treated in this way showed satisfactory laundering and wear performance in practical trials.

Introduction

The production from synthetic fibers of garments which can be washed and worn without ironing has stimulated research on developing similar effects in fabrics made from natural fibers.

Successful results have already been obtained with cotton, where fabrics with wash and wear properties have been commercially available for some time. The material is treated with synthetic resins which stabilize the fabric shape and surface texture during washing. In such treatments, internal polymer deposition stabilizes and inhibits creasing of individual fibers.

The problem is more complex with wool than with cotton, due to the added effect of felting, which causes shrinkage and surface distortion of a fabric. Satisfactory methods are now available for overcoming felting shrinkage in wool, among which are resin treatments. In the latter, however, polymer deposition is mainly on the surface of the fibers and, although this can eliminate felting, it has little or no effect on the dimensional stability of individual fibers in the material. Woven fabrics made from shrinkproof wool, therefore, still must be ironed after washing, even when a resin treatment has been used.

In considering wash and wear, it is important to define just what is meant by the term. A survey of the literature reveals a great variation in what is expected by different individuals in the performance of garments designated "wash and wear." The present trend is to class garments as requiring "no ironing," "little or no ironing," or "touch up." Consideration must also be given to the type of laundering treatment to which the garment will be subjected, and it is now customary to rate garment performances on the basis of four washing and drying procedures:

1. Hand wash—drip dry
2. Machine wash—drip dry
3. Machine wash—spin—hang dry
4. Automatic wash and wear (machine wash—tumble dry)

Apart from usual fabric properties such as strength, handle, colorfastness, and wear and pilling resistance, there are certain additional features needed in a garment to be classed as wash and wear. These are dimensional stability and retention of appearance in washing, stability of creases and pleats in both wear and washing, and retention of appearance during wear.

In making satisfactory wash and wear garments, it is now well known that stitchings, trimmings, linings etc. must be carefully selected and sewn to prevent any possibility of their causing gross distortion of the garment during washing. Such considerations are common to all wash and wear fabrics irrespective of fiber composition. Satisfactory procedures are now available for minimizing their effects and these will not be described here. The present work concerns the production of washable non-iron all-wool fabrics with the features outlined above.

In order to confer washable non-iron properties on wool, the major requirements are:

1. A shrinkproofing treatment: low or zero felting shrinkage is necessary.

2. Minimum relaxation shrinkage: finishing procedures must be carefully controlled to minimize subsequent relaxation.

3. Stabilization to retain surface appearance during laundering: it is essential to eliminate the surface wrinkling and puckering which occurs when wool fabrics are washed.

4. Retention of creases or pleats in garments such as trousers and skirts: this is closely related to requirement No. 3 and can now be obtained by the Si-Ro-Set [1] process [10].

5. Improvements in wrinkle resistance and recovery at high humidities.

Satisfactory commercial procedures are available to give all-wool fabrics some of the above properties.

Wrinkle resistance and recovery are partly related to fabric structure, and satisfactory behavior can be obtained by using suitable cloths. Despite this, there is still the need to improve this property in wool at high humidities, particularly in fabrics of minimum care.

Retention of appearance after laundering is perhaps the major obstacle to be overcome in obtaining washable non-iron effects in wool. Relaxation of strains, swelling, and the resultant low resiliency make wool susceptible to wrinkling during washing, so that a woven wool fabric after laundering and drying can be extremely puckered and mussy. Some form of setting treatment is therefore required for wool fabrics to retain their appearance after washing.

The ability of wool fibers to take a permanent set was first observed by Astbury and Woods [3]; the underlying mechanism has been studied by many workers, particularly by Speakman and his colleagues [8, 22, 23, 25]. This work was the basis for defining optimum conditions for setting wool fabrics with water and buffer solutions [13] and also led to procedures for permanent pleating and for setting of crepes [24].

Recent work by Farnworth [9] showed that a very rapid and high degree of permanent set can be imparted to wool fibers by boiling solutions of reducing agents. The underlying mechanism is considered to be rearrangement of hydrogen bonds following the scission of some cystine linkages. The Si-Ro-Set process [10], which involves spraying fabric with a dilute solution of a reducing agent immediately before the steaming operation in creasing or pleating, followed directly from this work.

[1] Si-Ro-Set is the subject of trade mark applications by C.S.I.R.O.

TABLE I. Details of Construction of Fabrics

Fabric	Warp yarn	Weft yarn	Picks/in.	Ends/in.	Weight, oz./sq. yd.	Weave
A	2/48's	2/48's	41	45	4	Plain
B	2/36's	1/18's	58	73	8	2/2 twill
C	2/48's	2/48's	71	84	8	Imitation double plain
D	2/24's	2/24's	38	46	9	Plain
E	2/48's	2/48's	80	88	9	2/2 twill
F	2/36's and 2/2/36's end and end	As warp	38	43	9½	Plain
G	2/40's	2/40's	67	75	8½	2/2 twill
H	3/36's	3/36's	40	44	9	Plain
J	2/48's and 2/2/48's end and end	As warp	44	52	9	Plain
K	2/32's	1/16's	44	52	7½	Plain
L	2/36's and 2/2/36's end and end	As warp	39	42	10	Plain
M	2/48's	2/48's	53	59	5½	Plain
N	2/24's end and end	2/24's end and end	31	47	9	Plain
O	2/40's	2/40's	44	53	6	Plain
P	2/48's	2/48's	53	59	5½	Plain
Q	2/36's	2/36's	38	42	8½	Plain
R	3/30's	3/30's	30	35	8½	Plain

In addition to setting creases and pleats, it was observed that Si-Ro-Set treatment preserved the surface appearance of fabric on wetting. This suggested using the process on shrinkproofed trousers and pleated skirts to set the entire garment and thus obtain washable non-iron effects.

With skirts pleated in pleating patterns, this would be a satisfactory approach because the fabric must be sprayed all over with thioglycollate solution, and normal production methods are such that adequate steaming can be given. However, there are more difficulties associated with such an approach when dealing with trousers or with skirts pleated on a steam press. It is an extremely tedious procedure to spray an entire garment and to give every portion of it the steaming required for the Si-Ro-Set treatment. Furthermore, production methods are such that it would not be possible to increase the steaming time beyond the 40–50 sec. used with Si-Ro-Set, and while this is adequate for producing creases of satisfactory durability, it would hardly be sufficient for the more rigorous requirements of stability in laundering.

Apart from the particular instances of trousers and pleated skirts, the Si-Ro-Set treatment also suggested the possibility of flat setting during blowing in the mill to enable fabrics to retain their appearance on washing.

The present paper describes experiments in which setting treatments have been applied to shrinkproofed woven wool in both fabric and garment form and evaluates the products for washable non-iron properties.

Fabrics

All-wool worsted cloths were used. The details of their construction are given in Table I.

Methods of Test

Appearance after Laundering

In evaluating fabrics for laundering stability, it is important to standardize the washing procedure and the illumination for examining the fabrics.

The washing procedure was to immerse the fabric (usually 15 in. square) in a 0.2% solution of anionic detergent (Teepol) at 40° C. and agitate gently by hand for 3 min. During this period, the fabric was removed, squeezed very tightly in the hands, and replaced in the solution. This squeezing was repeated five more times. Following the final squeeze, it was replaced in the solution, left for a further 2 min., removed, and hung from one edge in still air at room temperature. When dry, the fabric was removed and evaluated.

The standard lighting specified in the AATCC Tentative Test Method for wash and wear fabrics [1] was used for the evaluation. No attempt was made to place a grading on every sample. They were classified as being satisfactory if they were better than Class 5 of the standard photographs, which is the highest grading in the AATCC Test.

Relaxation Shrinkage

Fabrics 12 in. square were allowed to come to equilibrium with a standard atmosphere of 65% RH and 68° F. After measuring warp and weft dimensions, they were immersed in a 0.2% solution of a nonionic detergent (Lissapol N—I.C.I.) at 50° C. for 30 min. They were then removed, laid flat, and allowed to recondition in the above atmosphere before remeasuring.

Felting Shrinkage

Fabric samples 6 in. square were washed for given times in a domestic tumbler-type washing machine. Nonfelting ballast was used to make the total load up to 1000 g. Area shrinkage was calculated from warp and weft dimensions before and after washing.

Wrinkle Resistance and Wrinkle Recovery

Wrinkle recovery was measured by the ASTM standard method [2] except that a 4½-lb. weight was used to increase the severity of the test.

Recovery angles were measured after 1 min. and after 5 min. The shorter recovery time was intended to give some indication of wrinkle resistance, while the longer period is that normally used for determining wrinkle recovery. This differentiation is purely arbitrary.

Measurements were made at 68° F., at both 65% RH and after wetting out in water and squeezing between filter papers. The latter indicated possible wrinkling behavior at high RH; figures from such measurements agreed closely with those obtained at 92% RH.

Measurements made on damp fabrics should also give information on the ability to resist wrinkling during washing and to shed wrinkles during drying.

Bursting Strength

This was determined with a standard Mullen type Bursting Strength Tester on fabrics conditioned at

65% RH and 68° F. and after wetting in 0.2% Teepol.

Rate of Wetting

For comparing the wettability of treated and untreated fabrics, a modification [11] of the Draves test [7] was used. Strips of fabric 8 × 1 in. replaced the hanks normally used; the weight of the hook was 0.5 g. Collection of bubbles at the top of the fabric strip leads to long sinking times and variable results. However, this was overcome by cutting off the top corner of the strip. The angle at which this cut is made is critical, so that it is necessary to cut all samples with a template. An angle of 40° to the long edge of the strip was used in this present work. The tests were carried out in water at room temperature.

Shrinkproofing Treatments

Chlorination processes are still the cheapest and most widely used shrinkproofing treatments; properly applied and controlled, they give adequate shrink resistance with little adverse effect on the fibers [12, 27, 20]. Two of the main disadvantages of acid chlorination are unevenness and harshening. A recent, improved method [19] utilizes the effect of concentrated sodium chloride solutions in protecting wool from degradation [18], the chlorine being liberated at an easily controllable rate by the addition of oxidizing agents. Less active chlorine than usual is required for a given degree of shrink resistance. This method has been used in most of the present work and will be referred to as chlorination. Other methods studied to a lesser extent were permanganate-hypochlorite [26], permonosulfuric acid [21], polyamide-KOH [6], and peracetic acid-hypochlorite [5].

Fabric Setting

Experiments were carried out extending the use of reducing agents to the flat setting of shrinkproofed fabrics. In this work, the fabrics were impregnated with the setting reagent and immediately steamed on a blowing machine. Optimum conditions of treatment were determined on fabric A, which could be classed as having a low probability of giving a satisfactory wash and wear effect [14].

Choice of setting reagent. The mechanism proposed by Farnworth [9] indicates the importance of water in setting wool, as it is responsible for the rearrangement of hydrogen bonds. This fact was borne out in the development and practice of the Si-Ro-Set process [10], which depends on the simultaneous action of a reducing agent, water, and heat. In choosing a suitable reducing agent for use by clothing manufacturers in durably creasing woolen garments, the major considerations were speed of reaction, cost, and provision of either a ready-for-use reagent or one which required only dilution with water.

The work on fiber setting [9] showed ammonium thioglycollate at pH 7 to be slightly faster than sodium bisulfite and, although considerably more expensive than the latter, the amounts used in spraying garments for creasing or pleating were such that the chemical cost was very small. Furthermore, the supply of concentrated solutions of ammonium thioglycollate was well established for hair waving. A disadvantage of this reagent is formation of a highly-colored complex with iron, but this was easily overcome by using plastic or glass containers and nonferrous spray equipment.

The conditions and requirements for mill treatment of entire pieces are very different. Time is not so critical; steaming times of several minutes are possible in contrast to the seconds normally used in pressing garments. Moreover, the difficulties of keeping the solution and the wet fabric free from contamination with iron are much greater under normal industrial conditions than in spraying individual garments.

Because of these factors, sodium bisulfite has much to commend it as a setting agent for mill use in preference to thioglycollate. Trials carried out using each reagent gave comparable results.

Application of setting reagent. In all the present trials, the setting agent was applied by means of a pad mangle, followed immediately by blowing on a Whiteley dry steam blowing machine.

As an alternative to padding, the fabric could be wet out in the solution and then squeezed or hydroextracted, but this has the disadvantage of giving an uneven distribution of solution unless squeezing is carried out in open width.

These methods leave about 50% of solution on the weight of the wool, which is perhaps more than is necessary, as it was established that 40% was sufficient to obtain an adequate degree of crease setting in the Si-Ro-Set process [10]. A lower application

could be made by incorporating an open width spray over the fabric as it is fed into the blowing machine, but this involves modification to the existing plant.

Where chlorination is used for shrinkproofing, it should be possible to squeeze immediately after the bisulfite antichlor treatment and blow without rinsing. However, this would require close control.

Optimum setting conditions. Impregnation with the pad mangle was standardized so that solution uptake was about 50% of the conditioned weight of the fabric. Steam pressure throughout was 60 lb./sq. in. gauge. Samples of fabric A, 15 in. square, both untreated and shrinkproofed, were set with varying concentrations of setting reagent, steaming time, and acid content of the wool.

Evaluation of the fabrics for appearance on washing after these various treatments led to the following conclusions:

1. The minimum steaming time for reasonable results is 2 min., but best results are obtained on steaming for 3–5 min.

2. The minimum concentration of bisulfite is 0.5% (wt./vol.), but better results are obtained with a 1% solution. There is no advantage in increasing the concentration above this value.

3. Although the best setting treatments applied to untreated fabric gave an appearance rating equal to Class 5 of the AATCC grading, far better results were obtained on fabrics which had been shrinkproofed, even on very mild laundering. The reason for this is not obvious. It might be due to the micro felting which Makinson has shown to destroy creases and pleats long before any felting is visible to the eye [17]. Alternatively, it may be that some of the small fiber movements related to fabric relaxation have ample opportunity to occur during the prolonged aqueous treatments associated with shrinkproofing, whereas they do not take place during the relatively short setting process.

4. Fabrics should be nearly neutral prior to setting, inferior results being obtained when too much acid is retained from processes such as piece dyeing or acid chlorination. In view of effects on handle, discussed later, the optimum pH of shrinkproofed wool before setting is probably 4.5 to 6.0.

Properties of Treated Fabrics

A range of worsted fabrics each 10 yd. in length was chlorinated as described by McPhee [19] and set under the optimum conditions ascertained above —50% uptake of a 1% solution of sodium bisulfite and blowing for 5 min. Samples of fabric A were also given different shrinkproofing treatments prior to setting. All fabrics were then subjected to the methods of test previously described.

Appearance after Laundering

All of the chlorinated and set fabrics were appreciably better than Class 5 of the standard photographs, and all would be acceptable as washable non-iron fabrics for the laundering method used. Figure 1 shows typical fabrics after laundering when viewed under the standard lighting for the AATCC Test Method [1] to accentuate surface irregularities. Figure 2 shows the same fabrics in normal lighting.

The appearance of the fabrics treated with various shrinkproofing agents was found to vary somewhat. Permanganate-hypochlorite and chlorination each gave slightly better results than permonosulfuric acid, peracetic-hypochlorite, and polyamide-KOH, but all fabrics were better than Class 5. A fabric set without prior shrinkproofing was inferior to all the others but was graded Class 5.

It must be emphasized that these results were obtained on fabric A; it is certain that results better than these would be obtained on fabrics with a greater probability of taking a washable non-iron finish, such as multicolored geometric patterns, stripes, and checks [14].

Handle

The setting of normal fabrics by padding with bisulfite or thioglycollate and blowing while wet resulted in a softening of handle, probably due to the fabric having a smoother surface with fibers set flat. A similar effect was found when fabrics which had been shrinkproofed with permonosulfuric acid were set in this way. However, with some shrinkproofing treatments, marked stiffening occurred during setting. This could be removed by shaking, tumbling, or passing the dry fabric through rollers, after which the fabrics handled the same as before setting. The stiffening was found to return on wetting-out and redrying the set fabrics. The effect is gradually lost on washing the fabrics but may persist for several washing and drying cycles. The stiffening appears to depend on the pH of the wool during setting and apparently does not occur if the fabric pH is less than 6. Thus it would appear necessary to bring the wool to pH 4.5–6.0 after shrinkproofing to ensure satisfactory setting and a good handle.

With shrinkproofed fabrics which require softening, the softening agent can be used in the setting solution to be padded on before blowing. Many softeners precipitate in the solution, but satisfactory results have been obtained with the cationic surfactants Sapamine OC, Sapamine WL, and Cirrasol OD.

Wrinkle Recovery

Tables II and III show wrinkle recovery results for all the different conditions of setting and different methods of shrinkproofing.

The most significant feature of these results is the marked improvement in wet recovery of the treated fabrics; it, in some cases, approaches that of the original untreated fabric at 65% RH. This is a very desirable change, as it indicates an enhanced ability of the fabric to shed wrinkles at high RH and after laundering. The 1-min. recovery figures show the same trend as the 5-min. recoveries, which might indicate an improvement in wrinkle resistance at high humidity. However, as pointed out previously, the measurement of the wrinkle resistance–recovery relationship is purely arbitrary. Table II shows

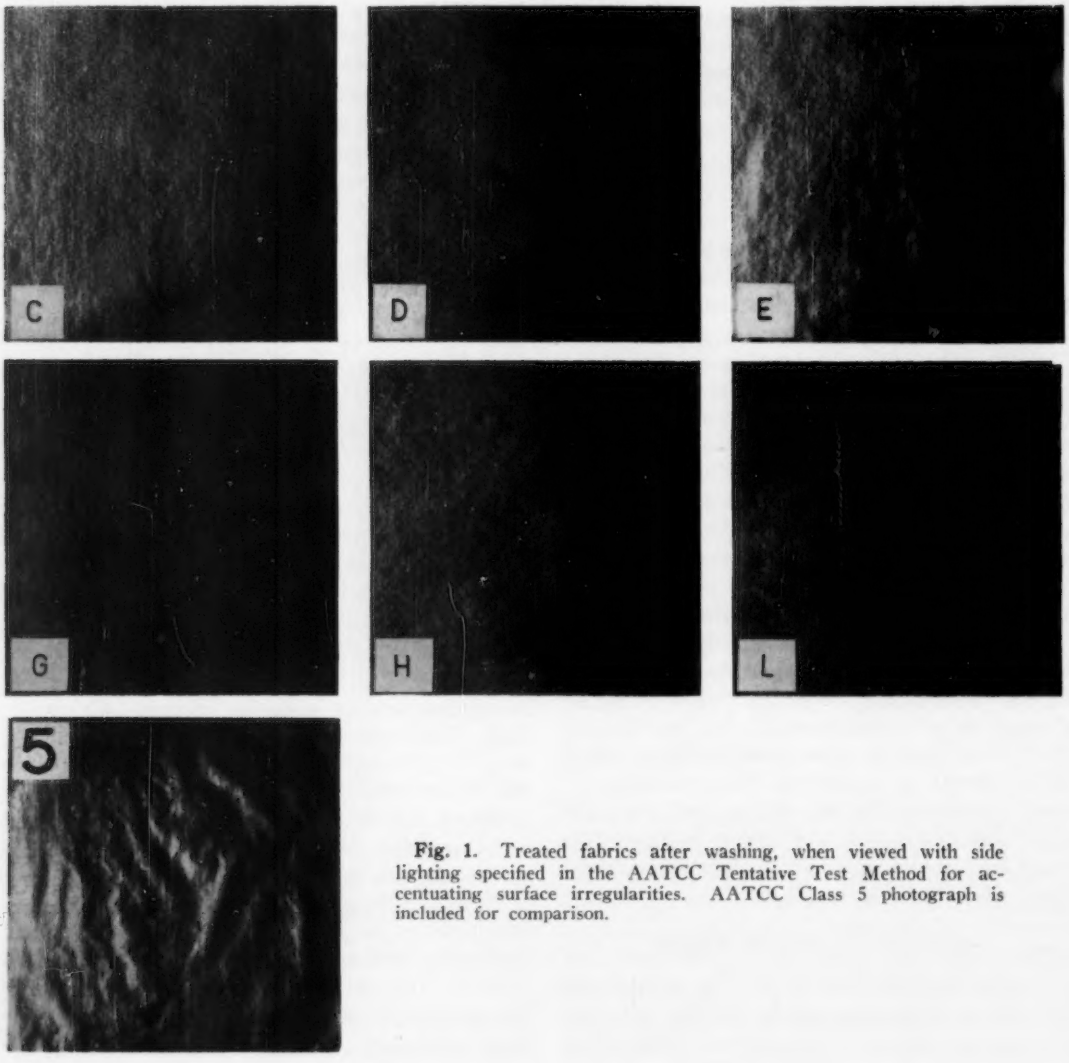

Fig. 1. Treated fabrics after washing, when viewed with side lighting specified in the AATCC Tentative Test Method for accentuating surface irregularities. AATCC Class 5 photograph is included for comparison.

that this effect is not confined to the combined shrinkproofing-setting procedure; the fabrics set without shrinkproofing show the same behavior. It is not possible, therefore, to explain the better performance of shrinkproofed-set fabrics after laundering on the basis of improved wrinkle recovery.

Tables II and III also show that in some cases the wrinkle recovery at 65% RH is reduced by the shrinkproofing-setting treatment. Fortunately, the effect in general is not large and the treated fabrics still retain the satisfactory performance of wool in this respect.

Relaxation Shrinkage

Table IV gives the relaxation shrinkages of a range of treated fabrics and it is seen that, in general, they retain a small amount of shrinkage. This is probably desirable, as garment makers, particularly tailors, rely on a certain amount of shrinkage to shape a garment.

Such small shrinkages would perhaps be expected, because measurements showed that relaxation occurred during the setting treatment, particularly when the setting solution was applied. As most fabrics are sold at a standard width, allowance for this shrinkage would have to be made in manufacturing the cloth, either in weaving or in finishing.

Felting Shrinkage

Table V gives the felting shrinkage of fabric A after shrinkproofing by various methods; Table VI shows the felting shrinkages of various fabrics chlorinated as described by McPhee [19].

Bursting Strength

Tables VII and VIII show the effects of shrinkproofing and setting on wet and dry bursting strengths when using different setting methods and a range of fabrics.

Shrinkproofing alone has little effect on bursting strength; setting alone reduces it but not to the same extent as the combination of the two treatments. Steaming in the presence of water has a similar effect to bisulfite solution.

In general, it appears that shrinkproofing followed by setting results in a decrease of 5–10% in the bursting strength of a fabric.

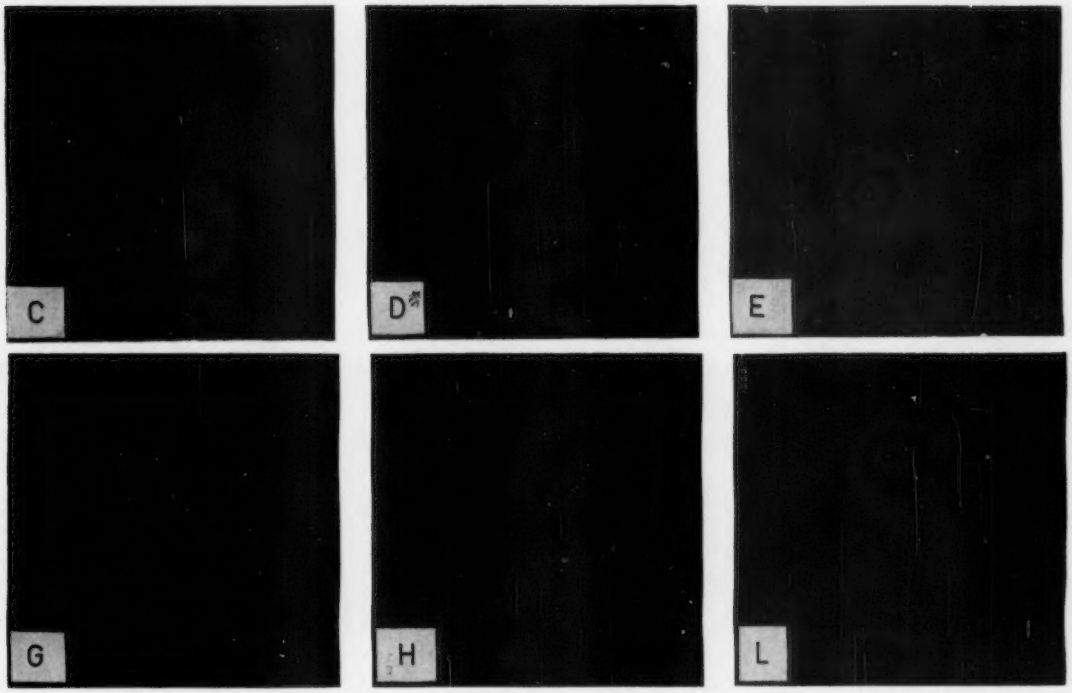

Fig. 2. Treated fabrics after washing, when viewed in normal lighting. The fabrics are the same as those in Figure 1.

Time of Wetting

The extent to which various shrinkproofing treatments destroy the natural water repellency of wool is shown in Table IX. Chlorination in salt solution destroys it completely, whereas permonosulfuric acid treatment has much less effect. Setting significantly reduces the time of wetting of normal wool and, except in the case of the permonosulfuric acid treatment, has a marked effect on shrinkproofed wools.

Cationic softeners reduce the rate of wetting [16], and the softeners referred to above as suitable for use in bisulfite solutions, as well as many others used for wool, have a similar effect on chlorinated wool. The result given in Table IX is an average for four samples of chlorinated wool each of which had been treated with a different softening agent.

Wearing Trials on Garments

The preceding results were sufficiently encouraging to carry out wearing trials on garments made from treated fabric.

In Australia, wash and wear has been largely confined to drip-dry shirts. Automatic washer-dryer combinations have not been available, which may be a major reason why there has been little development in wash and wear outerwear such as suits. It was decided therefore to carry out the initial trials on an all-wool fabric suitable for shirt-

TABLE II. Effect of Different Setting Conditions on the Wrinkle Recovery of Untreated and Shrinkproofed Fabric A

Setting reagent	Time of steaming, min.	Set only % Recovery after 1 min.	Set only % Recovery after 5 min.	Shrinkproofed with permanganate-hypochlorite and set % Recovery after 1 min.	Shrinkproofed with permanganate-hypochlorite and set % Recovery after 5 min.	Chlorinated in saturated salt and set % Recovery after 1 min.	Chlorinated in saturated salt and set % Recovery after 5 min.
		Recovery at 65% RH					
Original fabric		78	82	78	82	78	82
1% $NaHSO_3$	½	77	83	71	79	77	80
	2	76	83	74	77	73	76
	5	79	82	75	80	76	81
2% $NaHSO_3$	½	80	83	76	79	73	76
	2	77	81	74	78	72	74
	5	78	82	74	79	76	80
1% Ammonium thioglycollate	½	80	83	78	82	77	80
	2	78	81	75	78	81	82
	5	77	80	75	78	77	79
2% Ammonium thioglycollate	½	80	82	74	79	76	79
	2	77	81	74	79	77	80
	5	76	79	74	78	74	79
		Wet recovery					
Original fabric		60	65	60	65	60	65
1% $NaHSO_3$	½	61	69	62	68	64	68
	2	67	71	65	68	68	69
	5	73	77	68	70	71	72
2% $NaHSO_3$	½	64	68	60	61	69	71
	2	62	66	66	71	68	70
	5	72	76	74	78	72	77
1% Ammonium thioglycollate	½	74	76	68	69	68	74
	2	68	73	62	64	67	70
	5	72	75	67	70	67	69
2% Ammonium thioglycollate	½	68	71	68	71	65	68
	2	71	74	67	68	66	69
	5	70	74	70	73	68	72

ing. The only fabric approaching our requirements which was readily available was fabric M, which is about 50% heavier than normal cotton shirting. This fabric (60 yd.) was chlorinated in the piece and set on the blowing machine. Shirts of various sizes were manufactured from it without any further treatment and distributed among a group of observers, chosen at random. In addition, one shirt was successively hand-washed and drip-dried without any intermediate wearing for a total of 100 cycles. Another was subjected to 100 ¼-hr. washes in a tumbler-type washing machine with a full load, drip-drying after each wash. The appearance of both these garments was excellent, comparing more than favorably with any wash and wear shirt currently available. Towards the end of the trial, the shirt washed by machine was showing wear on the points of the collar and tending to pull away from the stitching across the yoke.

A summary of the opinions of wearers is given in Table X, and a photograph of one of the shirts which had been worn, hand-washed, and drip-dried more than 100 times without any re-pressing is shown in Figure 3.

Satisfactory results were reported; the garments could be classed as washable non-iron with high performance rating. The conditions of wear varied considerably from moderate use under office conditions to extremely hard outdoor wear on farms. As

TABLE III. Wrinkle Recoveries of a Range of Fabrics Before and After Chlorination and Setting

Fabric	Untreated % Recovery after 1 min.	Untreated % Recovery after 5 min.	Chlorinated and set % Recovery after 1 min.	Chlorinated and set % Recovery after 5 min.
	Recovery at 65% RH			
B	84	86	82	87
C	74	78	78	83
D	85	86	80	83
E	79	83	73	76
F	82	87	83	85
G	80	83	77	80
H	84	86	77	80
J	81	85	82	85
K	81	85	74	78
L	78	82	84	87
M	80	82	78	82
N	85	89	86	89
O	79	87	80	83
P	78	82	67	72
Q	81	84	75	79
R	84	88	78	82
	Wet recovery			
B	63	64	66	69
C	64	69	69	74
D	58	62	72	78
E	62	69	73	79
F	59	66	77	84
G	57	62	64	68
H	61	62	71	76
J	63	68	76	79
K	Twists too badly to obtain a value		Twists but approx. 100	
L	67	74	74	81
M	67	72	76	81
N	54	59	57	61
O	61	68	74	77
P	63	69	66	72
Q	58	62	70	78
R	Twists badly—approx. 44		69	73

TABLE IV. Relaxation Shrinkages of a Range of Chlorinated and Set Fabrics

Fabric	Relaxation shrinkage, % Warp	Relaxation shrinkage, % Weft
B	0.2	0.5
C	1.2	0.2
D	0.5	nil
E	1.0	−0.5*
F	1.5	0.2
G	nil	nil
H	0.7	nil
J	1.0	nil
K	0.5	−0.2*
L	1.5	nil
M	0.5	0.2
P	1.2	1.7

* Negative values mean an increase in length.

TABLE V. Effect of Various Shrinkproofing Treatments on the Washing Shrinkage of Fabric A

Shrinkproofing treatment	Area shrinkage, %, after washing for 1 hr.	Area shrinkage, %, after washing for 2 hr.
—	30	46
2% Chlorine (chlorination in saturated salt)	0	2
3% Potassium permanganate + 3% active chlorine at pH 8	0	1
2% Permonosulfuric acid	1	2
1% Peracetic acid + 2% active chlorine at pH 5.5*	8	14
1.5% Polyamide + 2% KOH in ethanol	0	1

* The optimum conditions for treatment were not found in this case.

can be seen from the table, the washing methods varied from hand washing to machine washing in several types of standard commercial appliances. The garments satisfactorily withstood shrinkage under all the conditions used, and the surface appearance was considered outstanding. In several cases wear was reported at the points of the collar, due mainly to abrasion in the washing machine. This is common with all shirts washed by machine and is not considered a criticism of the present fabric. In two instances, tears occurred at seams during machine washing. The manufacturer of the shirt considered this could be overcome by using wider seams. Apart from the above, there was no adverse criticism on the laundering performance of the garments. About half of the observers considered the fabric was too heavy in weight for summer wear. This is understandable, as the available material from which the garments were made was not intended originally

Fig. 3. Pure wool washable non-iron shirt after being worn, hand-washed and drip-dried more than 100 times without re-pressing.

TABLE VI. Washing Shrinkage on a Range of Fabrics Before and After Chlorination in Saturated Salt

Fabric	Area shrinkage in 3-hr. washing test, %	
	Control	Treated
B	29	4
C	31	5
D	21	6
E	12	3
F	13	4
G	36	6
H	29	7
J	9	3
K	18	7
L	12	3
M	30	6
N	25	8
O	16	7
P	24	5

TABLE VIII. Bursting Strengths of a Range of Fabrics Before and After Chlorination—Setting

Fabric	Bursting strength, lb./sq. in.			
	Untreated		Chlorinated and set	
	Cond.*	Wet	Cond.	Wet
B	156	109	142	100
C	139	102	126	85
D	141	97	140	94
E	140	101	142	101
F	128	94	128	86
G	149	105	142	105
H	148	105	145	100
J	121	90	117	89
K	135	93	129	87
L	132	95	126	92
M	107	78	104	72
N	134	98	133	92
O	115	87	112	84
P	111	81	105	75

* 68° F., 65% RH.

TABLE VII. Effect of Chlorination and Setting on the Bursting Strength of Fabrics A and Q

Steaming time: 5 min.

Setting reagent	Bursting strength, lb./sq. in.					
	Before chlorination			After chlorination		
	Fabric A		Fabric Q	Fabric A		Fabric Q
	Cond.*	Wet	Wet	Cond.	Wet	Wet
—	100	78	92	99	78	89
Steam only	95	77		94	71	
Water	93	73		84	66	85
1% Sodium bisulfite	93	69		87	63	81
1% Ammonium thioglycollate	91	72		90	65	84

* 68° F., 65% RH.

as shirting. Experiments are now in progress with lighter weight material.

Some trials have been carried out on trousers and skirts made from shrinkproofed-set fabric with satisfactory results. The usual difficulties of puckering at seams and zippers due to incorrect sewing tension, shrinkage of cotton etc. have been experienced. It is necessary to Si-Ro-Set creases, hems, and seams, although preliminary results suggest that this can be done simply by applying water prior to pressing. However, more work is required on this aspect of the investigation.

One trial has been made with shrinkproofed fabric, using the Si-Ro-Set pleating process as the setting treatment. Again the result was satisfactory, the pleats and the general appearance of the fabric being retained after laundering and drip-drying.

The trials with the shirts and the preliminary trials with other garments lead us to believe that satisfactory washable non-iron garments can be produced from all-wool fabric. Further experiments and trials are now in progress.

TABLE IX. Time of Wetting of Fabric A After Shrinkproofing and Setting

Shrinkproofing treatment	Time of wetting, sec.	
	Shrink-proofed	Shrink-proofed and set
—	70	40
Chlorinated	instantaneous	instantaneous
Chlorinated and softened	23	5
Permanganate-hypochlorite	10	3
Permonosulfuric acid	37	35
Peracetic acid-hypochlorite	17	7
Polyamide-KOH	5	2

TABLE X. Results of Wearing Trials on Wash and Wear Shirts

Observer	No. of wearings*	No. of washings*		Machine type†	Shrinkage	Reported appearance after drip-drying	Additional comments
		Machine	Hand				
1	42	6	6	1	Nil	Most satisfactory	Little soiling; could be worn 3 to 4 days per wash
2	10	10	—	1	Nil	Excellent	
3	60	30	—	2	Nil	Excellent	
4	30	15	—	1	Nil	Improved if anything by washing	Collar appearance after washing particularly good
5	42	14	—	2	Nil	Looked freshly ironed	Signs of abrasive wear on collar tips from machine washing
6	130	125	5	1	Nil	Excellent	Some signs of collar wear, otherwise still in excellent condition
7	63	2	31	1	Nil	Less wrinkled than no-iron cotton	Elasticity of fabric a good feature
8	20	10	10	1	Nil	Good	Cleans easily; small tear at sleeve seam
9	36	14	22	1	Nil	Some wrinkling around pocket	Collar keeps shape well; 6–8 hr. to dry indoors
10	7	3	3	1	Nil	Good	
11	15	14	1	2	Nil	Satisfactory	
12	34	18	16	—	Nil	No wrinkling	Collar stability a pleasing feature
13	32	32	6	1	Very slight	Very satisfactory	Wet creases are eliminated on hanging to dry
14	50	—	50	—	Nil	Looks pressed if dried in relatively still air	
15	105	30	65	2	Very slight	Excellent	Lack of soiling a decided advantage
16	12	8	4	3	Nil	Excellent	Several seam tears on washing from stitching too near edge
17	110	—	110	—	Nil	Excellent	Performance highly satisfactory in every way

* Some figures approximate.
† 1 = agitator; 2 = rotating drum; 3 = circulating liquor.

Some Associated Problems

In addition to the problems and difficulties in obtaining the desired stability of the fabric which have already been mentioned, there are other factors which arise in connection with this method of treatment.

As the setting treatment must be carried out near the end of the finishing routine, the effect on dyes must be considered. Several dye manufacturers have published reports showing the fastness of their entire range of wool dyes to the Si-Ro-Set process [4], and it has been found that these ratings are very similar to those for sulfur stoving. It might be expected, therefore, that similar ratings would apply in setting with sodium bisulfite, but this would need to be verified.

The effect on blowing wrappers must be considered, as these are expensive. It is difficult to obtain information on this other than by actual use of the method, but strength measurements and experience so far suggest that there is little degradation.

After the setting treatment, the fabric is still slightly damp and, although it dries in the atmosphere within 15–30 min., it may be preferable to run the piece through the tenter immediately after blowing rather than hang it in open width on racks similar to those used in London shrinking.

It is well known that degradative methods of shrinkproofing destroy the natural water repellency of wool so that it wets out rapidly. This is a disadvantage of the treatment when applied to fabrics for suitings and other outerwear, and it may be necessary to incorporate some water-repellent agent in the treatment. Certain cationic softeners impart some degree of repellency; the results of Table IX suggest that one of the agents referred to in connection with handle could fulfil the functions of wetting agent for the solution as well as softener and water repellent for the finished fabric.

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The Action of Nitric and Hydrochloric Acids on Wool with Particular Reference to Supercontraction of the Fibers

W. G. Crewther and L. M. Dowling

Division of Protein Chemistry, C.S.I.R.O. Wool Research Laboratories, Parkville, N.2 (Melbourne), Victoria, Australia

Abstract

Treatment of wool with 40% (wt./wt.) HNO_3 at 0–30° C. for periods up to 18 hr. causes a decrease in sulfhydryl, disulfide, and tyrosine contents and an increase in free amino groups. An equivalent concentration of HCl under similar conditions causes an increase in free amino groups and, with the more severe treatments, a decrease in tyrosine content and an increase in disulfide content as estimated by the Shinohara method. Alkali solubility and trypsin digestibility are greatly increased by the acid treatments; the solubility in urea/bisulfite solution first decreases, then increases with increasing time of treatment. Both acids cause loss of weight of the samples treated for 18 hr. at 30° C.

Apart from a small increase in the initial rate, the kinetics of supercontraction of single fibers in solutions containing 1 *N* HCl and 4 *M* LiBr are not greatly changed by acid treatment, nor is the level of the final contraction greatly altered. In 6 *M* LiBr at pH *ca.* 6 the nitrated fibers contract very rapidly by 10–15%; the contraction is then greatly retarded until a slow second stage of contraction develops. With HCl-treated fibers the contraction is again slightly accelerated initially and later retarded, but the changes are smaller and the division into two stages of contraction less apparent. Treatment with HNO_3 causes the fibers to contract more rapidly at all levels of contraction in 4 *M* LiBr at pH *ca.* 8, and with the more severe treatments, the initial contraction is followed by a period of elongation and a second slow contraction. On the other hand, HCl-treated fibers contract rapidly to the final level of contraction, but this may be very small. With the more severe treatments in HCl, the initial contraction is followed by elongation to a length approximating the original.

The kinetics of supercontraction are discussed in terms of chemical and configurational changes in the fibers.

Introduction

Whewell and das Silva [29] have shown that the nitration of wool fibers by treatment with 40% (wt./wt.) HNO_3 for 18 hr. at room temperature results in loss of the ability to take set and in almost complete disappearance of the phenomenon of supercontraction when the fibers are stretched and released rapidly in steam. While examining the effects of pretreatments in acids on the thermal contraction of wool fibers in solutions of salts such as LiBr, we have observed a similar though less complete decrease in the level of supercontraction under certain conditions.

Whewell and das Silva suggest that the effect may be due to steric hindrance resulting from nitration of the tyrosine side chains of the proteins in the fibers. However, other explanations appear equally probable. For example, hydrolysis of peptide bonds can be expected under the conditions of acid treatment. If this occurs in a random manner, the probability of a bond being hydrolyzed in a section of peptide chain between two disulfide cross-linkages will be directly proportional to the length of the section. It follows that longer chain sections will be broken more frequently than short units and the mean length of chain between cross-linkages will decrease. If disulfide cross-linkages are chiefly responsible for limiting the extent of supercontraction, such hydrolysis would be expected to cause a decrease in the equilibrium level of supercontraction [9].

In addition, although steric effects may occur following nitration of the tyrosine residues, this substitution may also affect the strength of any hydrogen bonds involving the phenolic hydroxyl groups. The possibility that the proteins of the wool fibers have undergone configurational changes during the acid treatment, with consequent modification of their contraction properties, must also be considered.

In this paper an attempt is made to evaluate the effects of these factors on the thermal contraction of wool fibers in solutions of LiBr.

Materials and Methods

Corriedale 56's wool was cleaned by cold solvent extraction followed by water washing; samples were treated with 40% (wt./wt.) HNO_3 or HCl of equivalent molarity (28% wt./wt.). The periods of treatment varied from 1 to 18 hr. and temperatures of 0, 10, 20, and 30° C. were used. The samples were neutralized in 1% $NaHCO_3$, washed many times in distilled water, air dried, and conditioned at 20° C. and 70% RH. The kinetics of supercontraction of modified and unmodified fibers were determined at 98.5° C. by the method previously described [4] using solutions of LiBr in 1 *N* HCl or in 0.1 *M* buffers at pH 6 or pH 8. The salts used for buffering at these pH values were sodium succinate and sodium borate respectively. The curves for untreated fibers have been constructed from the mean values for 4–6 fibers, those for modified fibers from mean values for two fibers. Free bromine was removed from the buffered solutions by the addition of a few crystals of $Na_2S_2O_3$ [8]. The LiBr was B.D.H. Laboratory Reagent; the HCl, HNO_3, and buffer salts were of Analar quality.

The alkali solubility of the wool was determined by the method of Harris and Smith [12], the solubility in solutions of urea/bisulfite by the method of Lees and Elsworth [19], the disulfide content of acid hydrolysates by the method of Shinohara [26] and of wools without acid hydrolysis by the polarographic method of Leach [17], the sulfhydryl content by the polarographic method of Leach [17], and the free amino groups by use of a ninhydrin reagent [21].

The trypsin digestibility of the wool samples was determined as described previously [2], the wool samples being pretreated with buffer at pH 11.0 for 20 hr. at 30° C. In addition, the trypsin digestibilities of samples which had been treated with acid at 20 and 30° C. for 18 hr. were determined after pretreatment with acetate buffer at pH 4.0. The loss in weight during digestion has been calculated both as a percentage of the initial quantity of wool used and as a percentage of the amount of wool remaining after pretreatment in the alkaline or acid buffers. However, the method of calculation does not greatly affect the general pattern although it introduces quantitative differences; we have therefore expressed our results only as a percentage of the original wool weight.

The tyrosine content of the wool samples was determined by a modification of the method of Bernhart [1]. Samples of wool (10 mg.) were hydrolyzed in 1 ml. of 6 *N* NaOH for 6 hr. at 105° C., acidified with 1 ml. of 7 *N* H_2SO_4 and 1.5 ml. H_2O added, followed by 1.5 ml. of a solution containing 15% (wt./vol.) $HgSO_4$ in 5 *N* H_2SO_4. The mixture was heated for 10 min. in a boiling water bath, cooled, and 1 ml. of 7 *N* H_2SO_4 and 1 ml. of 0.2% $NaNO_2$ solution added. The solution was adjusted to 10 ml. with distilled water and the optical density at 520 mμ compared with a standard curve obtained from estimations with pure tyrosine. The development of color in the solutions was time-dependent; readings were therefore made after color development had reached a maximum level (10–15 min.). The method was found to be precise and gave good agreement with the known tyrosine content of amino acid mixtures. 3-Nitrotyrosine does not produce color with Bernhart's reagent nor does it interfere with color production by tyrosine.

Experimental and Results

Chemical Changes in Wool Treated with HNO_3 or HCl

Disulfide and sulfhydryl content. Maclaren, Leach, and O'Donnell [20] have shown that the disulfide groups of wool are not quantitatively converted to cysteic acid residues by the action of dilute peracetic acid. Intermediate oxidation products are formed which disproportionate during acid hydrolysis or on treatment with ammonia. As a result of disproportionation to disulfide and cysteic acid residues during acid hydrolysis, estimates of (—SS— + —SH) by the Shinohara method are higher than those by the method of Leach. In the latter method a known mass of wool is shaken for 24 hr. in a solution containing urea, sodium sulfite, gelatin, salts, and $HgCl_2$; the amount of Hg^{++} bound by —SH formed in the wool is estimated using the polarograph.

Both methods were applied to the estimation of (—SS— + —SH) in acid-treated wool in order to determine whether or not disulfide groups were oxidized and if so whether partially oxidized groups were present. It was found that peptide material passed into solution in the urea/sulfite/gelatin/salts solution used for the polarographic estimation; this soluble component of the nitrated wool was reduced at the mercury electrode in the absence of Hg^{++} and so contributed to the current.

The presence of this material did not affect the current produced by uncombined mercuric ions since the slope of the curve relating the current with the concentration of mercuric chloride was unchanged by the addition of the soluble wool component to the solutions if sufficient mercuric salt was present to react with all —SH groups in the soluble component. Combination of Hg^{++} with these groups did not affect the current carried by the peptide material. Furthermore, on titrating equal amounts of nitrated wool with varying concentrations of mercuric chloride under standard conditions, the current remained constant at low concentrations of $HgCl_2$, then assumed the usual slope relating current with Hg^{++} concentration when —SH groups on the wool and soluble peptide had been converted to the mercury complex. Hence, the amount of reducible material passing into solution is independent of the amount of mercuric chloride present and the current it carries is unaffected by its reaction with mercuric ions. The (—SS— + —SH) content of the wool could therefore be calculated using the formula:

$$\text{—SS— + —SH } (\mu\text{mole/g.}) = \frac{2(i_{bl} - i_d + i_{sol} - i_{res}) \times 10^4}{m(i_{bl} - i_{res})}$$

where i_{bl} = the "blank current" carried by a solution containing all reagents but not shaken with wool, i_{res} = the "residual current" carried by a solution containing all reagents except $HgCl_2$ and not shaken with wool, i_{sol} = the current carried by 20 ml. of solution containing all reagents except $HgCl_2$ after shaking with wool of mass m mg., and i_d = the current carried by 20 ml. of solution containing all reagents including 5×10^{-4} M $HgCl_2$ and shaken with wool of mass m mg.

Since 3-nitrotyrosine, like the soluble component of nitrated wool, is reduced at the dropping mercury electrode (− 1.0 V), it seems probable that nitrotyrosine groups in the soluble peptide are also reduced at the mercury electrode.

Application of the method to acid-treated wool provided the results shown in Table I. There was a progressive decrease in (—SS— + —SH) content with increasing time and temperature of treatment in HNO_2. The results obtained by the Shinohara method and by polarography corresponded within experimental error.

Treatment with HCl appears to slow the reaction of $HgCl_2$ with wool samples in sulfite solutions; the period of equilibration was accordingly increased from 24 to 48 hr. Under these conditions the (—SS— + —SH) content was found to be unchanged by treatment in HCl. Similar results were obtained with the Shinohara reagent, except in the case of wool which had been treated with HCl for 18 hr. at 30°; with this material a marked increase in (—SS— + —SH) was observed (Table I). As this was the only treatment in HCl which caused a major decrease in weight of the wool, it seemed possible that a sulfur-deficient component had been

TABLE I. Disulfide Content and Loss of Weight of Wool Treated With HNO_2 or HCl

(Means of two determinations)

Acid treatment		HNO_2-treated wool				HCl-treated wool		
Temp., °C.	Time, hr.	Wt. loss, %	–SS– (Shinohara), μM/g.	–SS– (Leach), μM/g.	–SH, μM/g.	Wt. loss, %	–SS– (Shinohara), μM/g.	–SS– (Leach), μM/g.
Untreated		—	510	498	32.6	—	510	482
0	18	—	472	450	—	—	491	465
10	18	—	424	391	23.0	—	513	481
20	18	2.2	366	365	20.8	1.1	505	485
30	18	17.0	365	355	15.0	16.6	567*	482
30	1	—	426	422	—	—	—	—
30	2	—	421	383	—	—	—	—
30	4	—	394	399	—	—	—	—
30	8	—	373	401	—	—	—	—

* Mean of four determinations.

TABLE II. Tyrosine Content of Wool Treated With HNO_3 or HCl

Acid	Temperature of treatment, ° C.	Tyrosine content (μM/g.) after treatment for 1 hr.	2 hr.	4 hr.	8 hr.	18 hr.
Untreated		284				
HNO_3	0	—	—	—	—	231
HNO_3	10	286	291	291	66	30.3
HNO_3	20	197	86	32.4	16.5	20.9
HNO_3	30	22.5	16.5	12.7	10.4	5.5
HCl	10	—	—	—	—	281
HCl	20	—	—	—	—	277
HCl	30	—	—	275	251	216

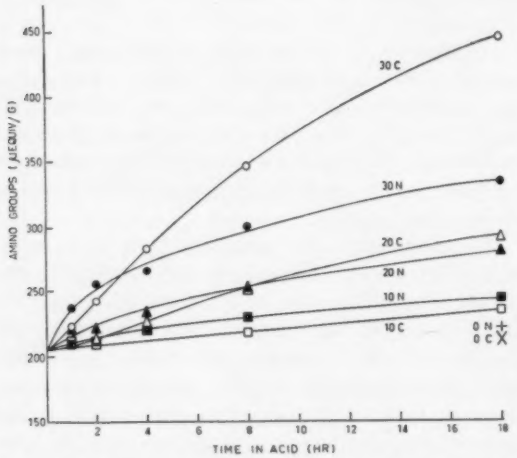

Fig. 1. Changes in primary amino groups of wool during treatment in 40% HNO_3 or 28% HCl. These acids are indicated by N or C respectively; numerals indicate the temperature of treatment in ° C.

leached out during treatment. In order to determine whether the discrepancy between the estimates by the two methods is due to the presence of partial oxidation products of disulfide groups, wool treated in HCl at 30° C. for 18 hr. was treated with 2 *M* KI/2 *N* HCl with a liquor ratio of 50:1 in the dark at 2° C. for 16 hr. The wool was thoroughly washed, air-dried, conditioned, and the disulfide content compared with that of the acid-treated material. No change in (—SS— + —SH) was obtained following this treatment; hence no appreciable amount of partially oxidized disulfide was present [15].

Table I also indicates that only a little more than half of the sulfhydryl groups of wool were oxidized by HNO_3 under the most severe conditions tested.

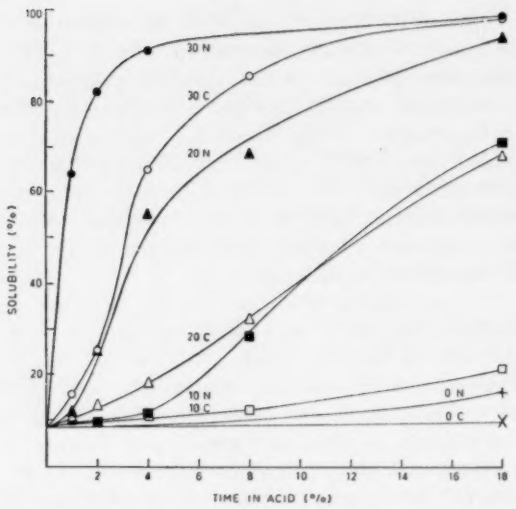

Fig. 2. Changes in the alkali solubility of wool during treatment with 40% HNO_3 or 28% HCl. These acids are indicated by N or C respectively; numerals indicate the temperature of treatment in ° C.

Tyrosine content. The decrease in tyrosine content of wool during its treatment with HNO_3 is shown in Table II. At 20 or 30° C., nitration of the tyrosine residues proceeded rapidly and almost to completion. At 10° C., on the other hand, the tyrosine content remained unchanged for 4 hr.; rapid nitration then took place. At 0° C., even after 18 hr. in HNO_3, less than 20% of the tyrosine residues were nitrated. Treatment with HCl at 30° C. also led to a reduction in the tyrosine content, but only under conditions resulting in loss of weight of the wool samples.

Production of free amino groups. A comparison of the rate of appearance of free amino groups during treatment with HNO_3 and HCl solutions (Figure 1) showed that the two solutions produced similar results at the lower temperatures used. However, at 30° C., although the rate of production of amino groups was initially greater in HNO_3 than in HCl, it decreased with increasing time of treatment.

Alkali solubility, trypsin digestibility, and solubility in urea/bisulfite solutions. As might be expected from earlier observations that the alkali solubility test and the trypsin digestibility (following pretreatment in alkaline buffer solution) are affected in a similar manner by acid treatment of wool [2], the patterns obtained by these two tests were very simi-

lar (Figures 2 and 3). Of particular note is the period of 4 hr. at 10° C., during which there was little change in alkali solubility, trypsin digestibility, or tyrosine content (Table II). Another notable result was the extraordinarily high trypsin digestibility of the acid-treated wool (30° C.) following pretreatment in buffer at pH 4; 50% for nitrated wool and 17% for wool treated with HCl (Figure 3). Figure 4 shows that during treatment with HNO_3 or HCl the solubility of wool in urea/bisulfite solution first decreased, then increased again to almost 100%, the rates at which these changes occurred being greatly dependent on temperature.

Kinetics of Supercontraction of Acid-Treated Wool

Supercontraction in solutions containing 4 M LiBr and 1 N HCl. The kinetics of supercontraction of wool fibers in acidic solutions of LiBr were so little changed by treatment with HNO_3 or HCl that the results of pretreatment in these acids at 30° C. only have been recorded here. Figure 5 shows that both acid treatments increased the initial rate of contraction, the effect being greater with HNO_3 than with HCl. The rate of the later stages of contraction was not greatly affected. For the purpose of this investigation, perhaps the most important observation is that the acid-treated fibers, like untreated fibers, continue to contract at normal rates even after the length has decreased by as much as 60%. The curves of Figure 5 represent mean values for two fibers, so that the maximum contractions obtained with individual fibers were greater than those recorded in the figure.

Supercontraction in 6 M LiBr at pH 6.2. The kinetic curves for contractions in 6 *M* LiBr buffered at pH 6.2 with 0.1 *M* sodium succinate show greater differences in the behavior of fibers treated with the different acids (Figures 6, 7, and 8). As the time of pretreatment in HCl increased, there was a progressive increase in the initial rate of contraction and a decrease in the level at which contraction ceased. The magnitude of these effects increased with increasing temperature. Treatment with HNO_3 caused even greater increases in the initial rate of contraction but, unlike the fibers treated with HCl, the initial contraction was followed by a period during which contraction almost ceased. The rate of the subsequent second stage of contraction was less than that of untreated fibers at a similar level of contraction. The second stage of contraction continued for periods of more than 100 min. There is some indication from the curves in Figures 7 and 8 that the level at which the first stage of contraction ends and the second stage becomes apparent at first de-

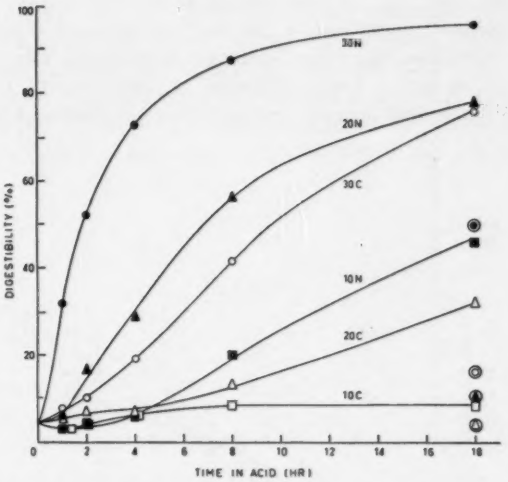

Fig. 3. Changes in the trypsin digestibility of wool during treatment with 40% HNO_3 or 28% HCl. These acids are indicated by N or C respectively; numerals indicate the temperature of treatment in ° C. Curves connect the values for digestibility after pretreatment at 30° C. for 20 hr. in 0.1 *M* piperidine at pH 11; circles enclose values for digestibility following pretreatment in 0.1 *M* acetate buffer at pH 4.

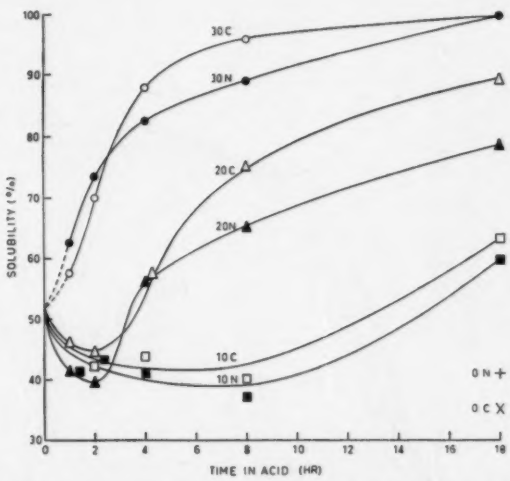

Fig. 4. Changes in the solubility of wool in urea/bisulfite solutions during treatment with 40% HNO_3 or 28% HCl. These acids are indicated by N or C respectively; numerals indicate the temperature in ° C.

creases and then increases with increasing time of acid treatment.

Supercontraction in 4 M LiBr at pH 8.4. Supercontraction of the acid-treated fibers at pH 8.4 presents yet another pattern of behavior (Figures 9, 10, and 11). Fibers treated with HCl showed a dramatic reduction in the level of the equilibrium contraction and a small increase in the initial rate of contraction. The magnitude of these effects increased with temperature and time of treatment in the acid solutions. Treatment in HCl at 30° for 8 or 18 hr. resulted in a marked increase in the initial rate of contraction and, compared with fibers heated for 4 hr., an increase in the level of the maximum contraction (Figure 11); this was followed by a period of rapid elongation to lengths which, with 18 hr. treatment, exceeded the original. On the other hand, treatment with HNO_3 under relatively mild conditions had little effect on the level of the maximum contraction, but the rate was greatly in-

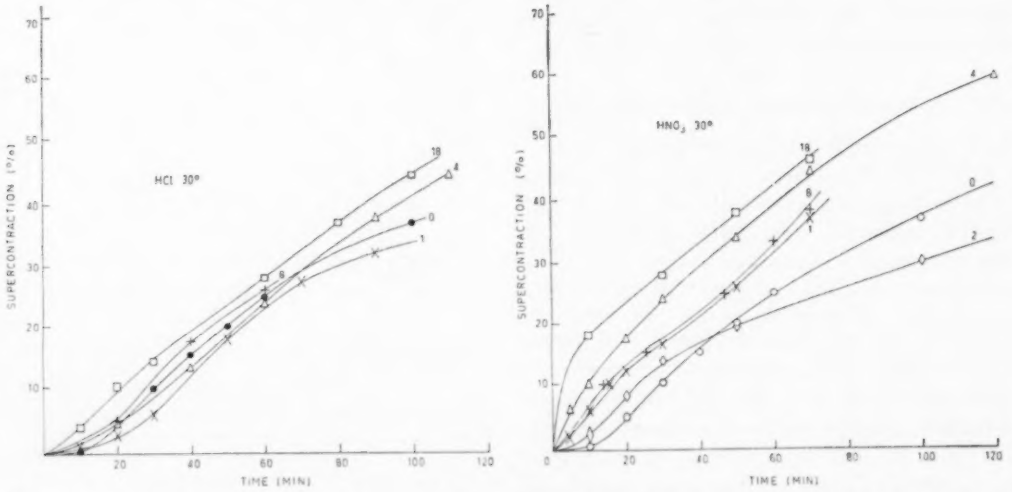

Fig. 5. The kinetics of supercontraction of untreated and acid-treated wool fibers in 1 *N* HCl/4 *M* LiBr. Numerals indicate the time in hours of treatment in 40% HNO_3 or 28% HCl at 30° C.

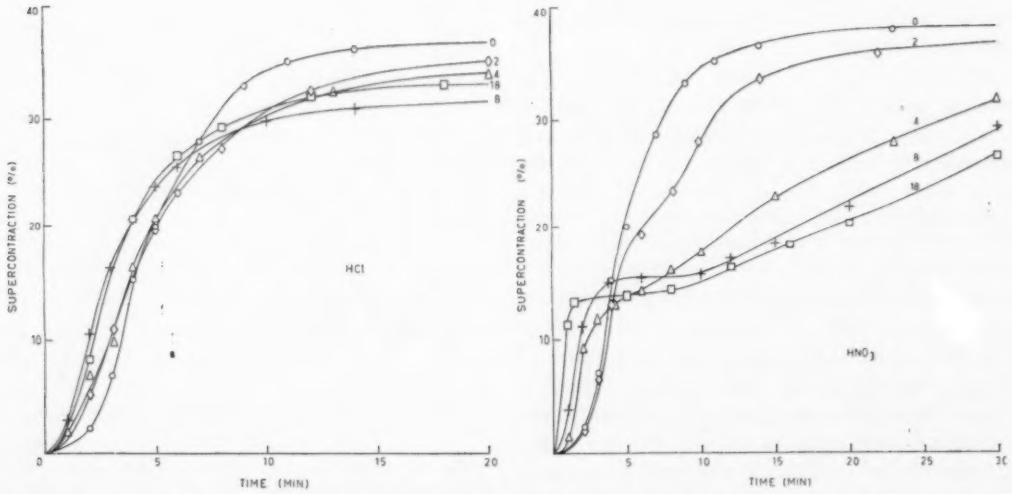

Fig. 6. The kinetics of supercontraction of untreated and acid-treated wool fibers in 6 *M* LiBr at pH 6.2. Numerals indicate the time in hours of the treatment in 40% HNO_3 or 28% HCl at 10° C.

creased at all levels of contraction. With progressively more severe treatment in HNO_3, the rate of contraction increased still further and the initial contraction was followed by elongation and a second slow contraction.

Contraction of acid-treated fibers in less concentrated solutions of LiBr. A further consequence of the action of HCl or HNO_3 on wool is a decrease in the concentration of LiBr required for rapid supercontraction of the fibers. At pH 8.3, wool treated with HNO_3 at 20° C. for 18 hr. contracted rapidly in 1 *M* LiBr and subsequently elongated (Figure 12), whereas untreated wool showed no significant contraction in 3 *M* LiBr at pH 8.3 during the experimental period. Wool treated with HCl at 30° C. for 18 hr. also contracted in 1 *M* LiBr at pH 8.3 (Figure 12), but much more slowly than the wool which had been treated with HNO_3 at this temperature for only 8 hr. Similarly, the contraction kinetics at pH 6.2 of wool treated with HNO_3 for 8 hr. at 30° C. were practically unchanged by reducing the LiBr concentration from 6 *M* to 4 *M* and a slow

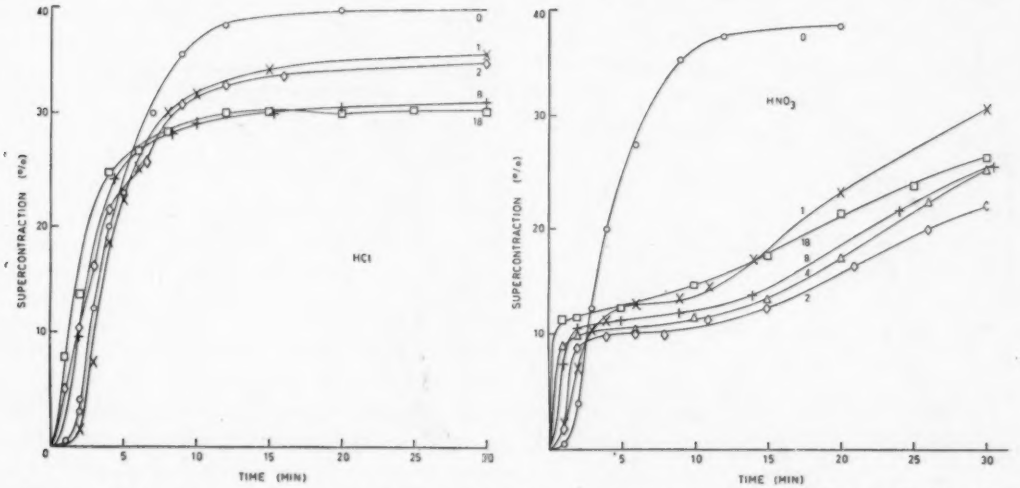

Fig. 7. The kinetics of supercontraction of untreated and acid-treated wool fibers in 6 *M* LiBr at pH 6.2. Numerals indicate the time in hours of the treatment in 40% HNO_3 or 28% HCl at 20° C.

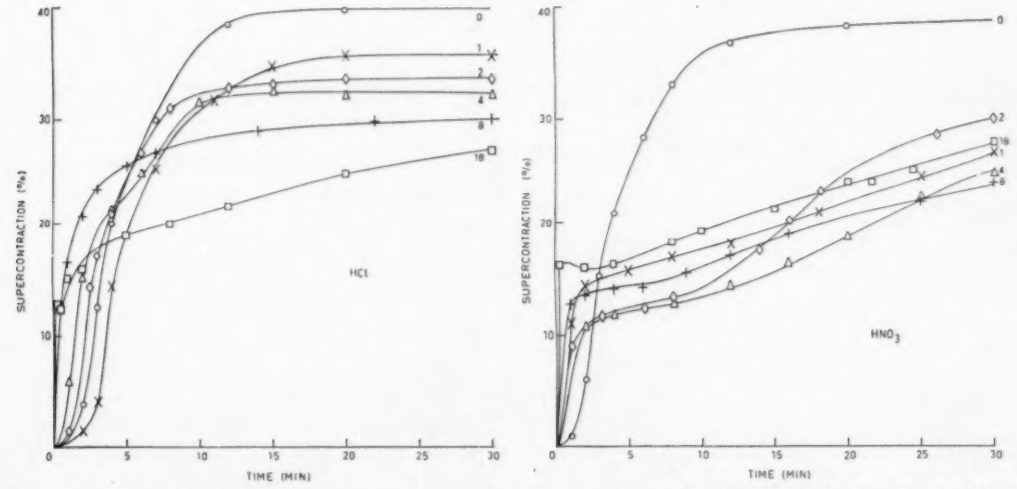

Fig. 8. The kinetics of supercontraction of untreated and acid-treated wool fibers in 6 *M* LiBr at pH 6.2. Numerals indicate the time in hours of the treatment in 40% HNO_3 or 28% HCl at 30° C.

contraction was obtained in 3 *M* LiBr (Figure 12), whereas untreated wool contracted very slowly in 5 *M* LiBr (Figure 12). Fibers treated with HCl for 4 hr. at 30° C. contracted rapidly in 5 *M* LiBr at pH 6.2 and slowly in 4 *M* LiBr. Similar effects were observed when the fibers were contracted in 1 *N* HCl containing LiBr. A noteworthy feature of the contraction kinetics of HCl-treated fibers at pH 6.2 is the appearance of a well-defined two-stage contraction on reducing the concentration of LiBr to 5 *M* (Figure 12).

Titration of Acid-Treated Wool

In seeking reasons for the difference in contraction behavior of nitrated wool at pH 6.2 and pH 8.4, it was important to determine whether nitrated wool contains residues which ionize over this pH range in solutions of LiBr. Two large samples of wool were treated with HNO_3 and HCl respectively at 30° C. for 1 hr. and washed with running distilled water to the isoionic point. After being air-dried and conditioned each sample of wool was made

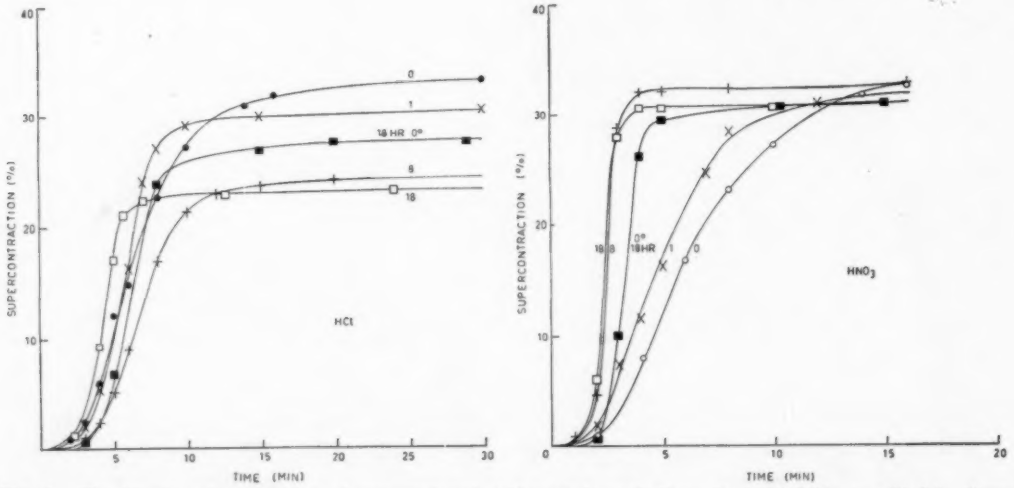

Fig. 9. The kinetics of contraction of untreated and acid-treated wool fibers in 4 *M* LiBr at pH 8.4. Numerals indicate the time in hours of the treatment in 40% HNO_3 or 28% HCl at 10° C. The curve for treatment at 0° C. for 18 hr. is also included.

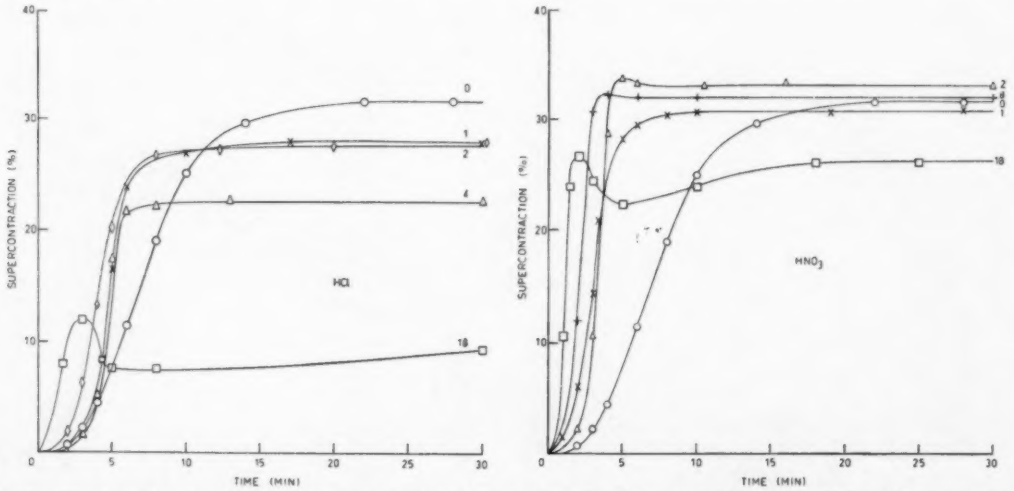

Fig. 10. The kinetics of contraction of untreated and acid-treated wool fibers in 4 *M* LiBr at pH 8.4. Numerals indicate the time in hours of the treatment in 40% HNO_3 or 28% HCl at 20° C.

homogeneous by hand carding; 10 samples containing 1 g. wool were taken from each. Two 6 *M* LiBr solutions were prepared containing sufficient KOH to give pH values near 6 after equilibration of 30 ml. with 1-g. samples of nitrated and HCl-treated wool respectively. From each solution 10 30-ml. aliquots were taken. Solutions of KOH were prepared such that addition of 15 ml. to 30 ml. of the LiBr solutions gave a pH slightly greater than 8 after equilibration with 1 g. of acid-treated wool; 0.009 *N* KOH was used for the HCl-treated wool and 0.028 *N* KOH for the nitrated wool. Graded amounts up to 15 ml. of these solutions were added to the appropriate 30-ml. aliquots of LiBr; the wool samples were then immersed in the solutions and shaken at 28° C. for 48 hr.

The pH values of the supernatant solutions were estimated using a soda-glass electrode and potentiometer. In this way a range of pH values from about 6 to 8.1 was obtained with a corresponding decrease in LiBr concentration from 6 *M* to 4 *M*. The recorded pH values are slightly lower than the actual values because no correction has been made for the effect of Li^+ on the glass electrode. However, measurements with the hydrogen electrode indicate that the errors are small; moreover, the values obtained are directly comparable with those recorded for the supercontraction experiments. Figure 13 shows that the number of groups reacting with the alkali over the pH range 6 to 8 is much greater in nitrated wool than in HCl-treated wool. The curve representing the titration difference for the two types of wool (Figure 13) indicates that nitration results in the formation of an ionizable group with an apparent pK_a near 6.8 in an amount approximating 200 μmole/g. Over the pH range 6.2 to 7.2 there was a marked change in color from khaki to reddish brown.

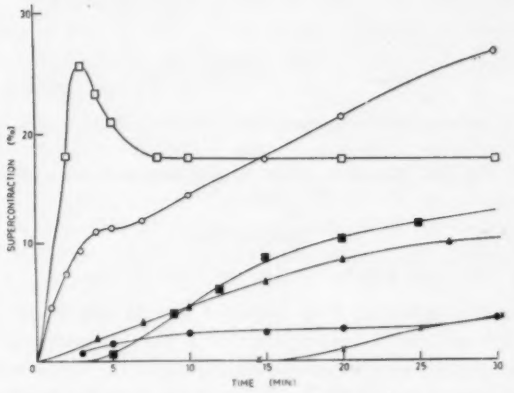

Fig. 12. The kinetics of supercontraction of untreated and acid-treated wool fibers in LiBr solutions at various concentrations. □ Fibers treated in HNO_3 18 hr. at 20° C.; 1 *M* LiBr, pH 8.3. ■ Fibers treated in HCl 18 hr. at 30° C.; 1 *M* LiBr, pH 8.3. ○ Fibers treated in HCl 4 hr. at 30° C.; 5 *M* LiBr, pH 6.2. ● Fibers treated in HCl 4 hr. at 30° C.; 4 *M* LiBr, pH 6.2. ▲ Fibers treated in HNO_3 8 hr. at 30° C.; 3 *M* LiBr, pH 6.2. × Untreated fibers; 5 *M* LiBr, pH 6.2.

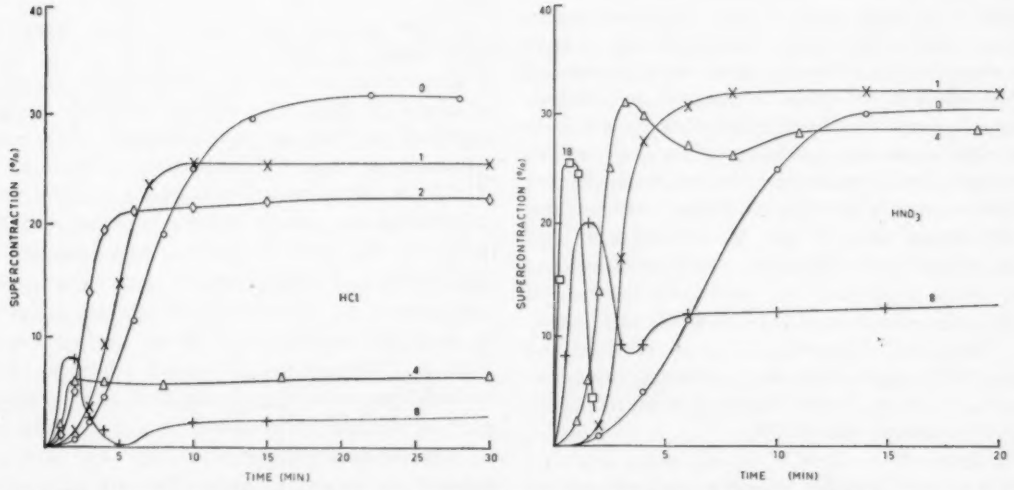

Fig. 11. The kinetics of contraction of untreated and acid-treated wool fibers in 4 *M* LiBr at pH 8.4. Numerals indicate the time in hours of the treatment in 40% HNO_3 or 28% HCl at 30° C.

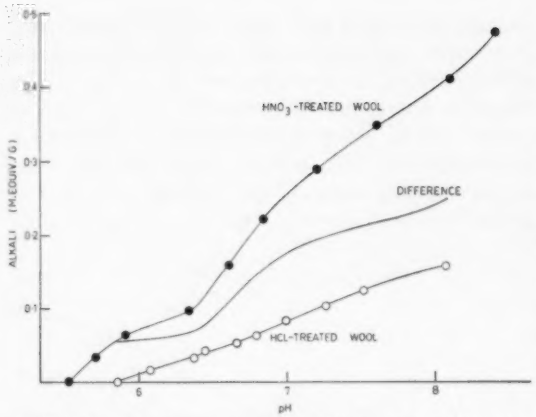

Fig. 13. Titration curves of HNO_3-treated wool and HCl-treated wool.

Discussion

Chemical Changes in Acid-Treated Wool

It is apparent from Tables I and II and Figures 1–4 that wool treated with 40% HNO_3 undergoes a number of chemical changes, some of which are also induced by HCl. We propose to consider the nature of these changes; later an attempt will be made to relate these to the behavior of the fibers during supercontraction.

The protein or peptide material dissolved during treatment with HCl at 30° apparently contains more tyrosine and possibly less cystine than the bulk of the fiber (Tables I and II); this suggests preferential hydrolytic attack on certain components of the fibers. Similar material may be extracted during treatment with HNO_3, but any change in tyrosine content which this may cause would be masked by the effect of nitration on the tyrosine content. Comparison with the nitration of other phenols indicates that, under the conditions of the experiments, mononitrotyrosine residues would be the chief product of the reaction of HNO_3 with tyrosine residues; 3-nitrotyrosine can in fact be identified in acid hydrolysates of nitrated wool. This substance has been shown to produce no color with the reagent used for the estimation of tyrosine in alkaline hydrolysates of wool. However, the work of Zahn and Fritze [30] suggests that the dinitro derivative may also be produced under the more extreme conditions of treatment with HNO_3.

Estimates of (—SS— + —SH) using acid hydrolysates corresponded within experimental error with those obtained with whole wool (Table I), even though a portion of the disulfide had been oxidized by nitric acid. Hence if partially oxidized disulfide groups are formed as a first step in the oxidation of disulfide by nitric acid [20], their further oxidation to cysteic acid residues must be rapid compared with the rate of the initial attack on the disulfide bonds. The data in Table I indicate that oxidation of disulfide bonds of wool by HNO_3 practically ceases when about 25% of the total disulfide has been oxidized. This may be due to differences in reactivity of disulfide bonds in different structures or sites in the fiber or to the establishment of an equilibrium.

Figure 1 indicates that HNO_3 hydrolyzes peptide bonds more rapidly than HCl under mild conditions of acid treatment, whereas with HNO_3 under the more severe conditions, the appearance of free amino groups is greatly retarded. This may be due to formation of HNO_2 by reaction of HNO_3 with —SH and —SS— groups and subsequent partial deamination of the wool proteins, or to direct oxidation of amino groups [30]. The increases in primary amino groups after treatment with HCl for 18 hr. at 0, 10, 20, and 30° C. correspond with the hydrolysis of 0.08, 0.31, 0.95, and 2.62 peptide bonds respectively per 100 peptide bonds in the original wool. The value of the energy of activation obtained from the effect of temperature on the initial rate of formation of amino groups, 24 Kcal./mole, corresponds closely with that obtained by Leach [16] for the liberation of aspartic acid from glycyl-DL-aspartic acid.

Gordon, Martin, and Synge [7] have shown that amide bonds are hydrolyzed by 10 *N* HCl at 37° C. at almost twice the rate of peptide bonds. Hence, if we accept the figure of 6.16% for the amide nitrogen expressed as "percent total nitrogen" [18], about 0.4 amide bonds should be hydrolyzed in 18 hr. at 30° C. per 100 peptide bonds in the original wool.

Modifications which increase the net negative charge of the wool by forming new anionic side chain groups, or which permit more extensive rearrangement by disrupting covalent bonds, result in increased swelling, disordering, and eventually solution of the proteins in alkaline solutions. Such modifications favor tryptic digestion after pretreatment in alkaline buffer solutions and also increase the alkali solubility of the wool [2]. The similarity between the results of these two tests (Figures 2 and 3) is therefore to be expected. However, the

very high values obtained for trypsin digestion following pretreatment in buffer at pH 4.0 (Figure 3) indicate that the proteins of the wool have been considerably disordered during the acid treatment, particularly with HNO_3.

Although the alkali solubility and trypsin digestibility of wool treated with HNO_3 at 10° C., like the tyrosine content, were practically unchanged during the first 4 hr. of treatment, the urea/bisulfite solubility was reduced from 53 to 41% in this period (Figure 4). The solubility of wool in solutions of urea/bisulfite has been shown to decrease when the wool is steamed or treated with alkali [19] and this has variously been attributed to the formation of lanthionine cross-linkages [19], to disulfide interchange resulting in conversion of intrapeptide disulfide bonds to interpeptide bonds [13], or to configurational changes in the wool proteins [23]. Under the conditions of the present experiments it is unlikely that lanthionine cross-linkages would be formed and, particularly in the case of treatment in HCl for 18 hr. at 30° C. with its concomitant increase in disulfide content as estimated by the Shinohara method (Table I), the chemical evidence discounts this possibility. The hypothesis that disulfide interchange takes place to form new cross-linkages is also difficult to support in view of the rapid contraction of the acid-treated fibers in acidic solutions of LiBr to levels approaching those for untreated fibers (Figure 5). The evidence, therefore, supports the view that the decrease in solubility of wool in solutions of urea/bisulfite is a reflection of configurational changes in the wool proteins. The very large increase in the urea/bisulfite solubility which follows the initial reduction in solubility (Figure 4) probably results from the rupture of covalent linkages. Lees and Elsworth [19] observed a similar increase in urea/bisulfite solubility after heating wool in solutions of acid. The decrease in solubility which precedes this effect has not been recorded previously.

The chemical effects of treatment with HNO_3 may be summarized as follows: (1) a decrease in the number of covalent linkages in the structure, (2) the formation of new anionic and cationic side chain groups resulting from peptide hydrolysis and the formation of new anionic groups as a result of amide hydrolysis and oxidation of disulfide cross-linkages, (3) a decrease in the pK_a values of side chain groups due to nitration of tyrosine residues and oxidation of sulfhydryl groups, and (4) configurational changes in the wool proteins.

Treatment with HCl causes changes (1), (2) excluding disulfide oxidation, and (4), though to a lesser degree than HNO_3; the pK_a values of side chain groups would not be affected.

Supercontraction of Acid-Treated Wool Fibers

In attempting to explain the effects of acid treatments on the kinetics of supercontraction of wool there are four main aspects of the work to be considered.

Effect of pH on the apparent equilibrium level of contraction. Although acid-treated fibers were very fragile when contracted in 1 *N* HCl/4 *M* LiBr and usually broke before reaching the equilibrium contraction, several fibers contracted 50–60% without diverging appreciably from the contraction kinetics of untreated fibers (Figure 5). If hydrolysis of peptide bonds had resulted in shortening of the mean length of the contractile units, a decrease in the level of equilibrium contraction would be expected [9]. It is probable, therefore, that peptide hydrolysis has occurred chiefly in noncontractile structures of the fibers, at centers of multiple cross-linking, or, since the length measurements recorded here refer to the *para*cortex [4], in the *ortho*cortex. Consequently, the very marked reduction in the equilibrium contraction of HCl-treated fibers in 4 *M* LiBr at pH 8.4 (Figure 11) is best explained in terms of configurational changes, particularly in the structure responsible for the second stage of contraction. The increase in the free energy of activation resulting from this modification is apparently sufficient to reduce the rate of contraction of the modified structure to insignificant levels. Such a change would be expected to proceed step-wise, and protein structures at intermediate stages of modification would be expected to contract at intermediate rates. In general, the curves for HCl-treated fibers (Figures 6–11) can be explained satisfactorily on this basis.

Since the modified structure contracts very slowly in 4 *M* LiBr at pH 8.4 (Figures 10 and 11) but contracts slightly more readily than the original fibers in 1 *N* HCl/4 *M* LiBr (Figure 5), it seems probable that the formation of new salt linkages after neutralization of the acid-treated wool or rearrangement of dipoles in the fiber proteins is responsible for stabilizing the modified structure.

The effect of pH on the kinetics of supercontraction of wool fibers treated with HNO_3. Since treatment with either HCl or HNO_3 accelerates the first stage of contraction at all pH values, the chief effects requiring explanation relate to the kinetics of the second stage of contraction. Comparison with fibers treated in HCl shows that at pH 6.2 fibers treated with HNO_3 contract much more slowly in the second stage, whereas at pH 8.4 the reverse is true. The chief chemical differences between these modified fibers—oxidation of —SS— and SH groups, and nitration of tyrosine side chains—readily account for the greater rate of contraction of HNO_3-treated fibers at the higher pH value. The former effect would decrease the number of covalent cross-linkages and so facilitate contraction; the latter effect, if the nitrotyrosine residues are ionized at pH 8.4, would increase the net negative charge on the proteins and also favor contraction [3].

The presence of cysteic acid residues cannot account for the difference in the kinetics of contraction of nitrated fibers at pH values 6.2 and 8.4, since they are completely ionized at both pH values. The factor most likely to account for this major difference in contraction behavior is the difference in the number of ionized tyrosine or nitrotyrosine side chains.

By analogy with the effect of nitration on the ionization of phenol, substitution of a nitro group *ortho* to the OH group of tyrosine residues would be expected to lower the pK_a to a value approaching 7 if the OH group is not involved in hydrogen bond formation. A pH titration curve gave a value of about 7.15 for the pK_a value of 3-nitrotyrosine. Further nitration to form 3:5 dinitrotyrosine residues would reduce the pK_a further to a value between 3 and 4. Figure 13 shows that nitrated wool contains ionizable groups with an apparent pK_a value near 6.8; these are not present in wool treated with HCl under similar conditions. The color change which took place in nitrated wool over the pH range 6.4 to 7.2 and the approximate correspondence of the number of titratable groups, 200 μmole/g., with the loss of tyrosine during nitration, 262 μmole/g., provide strong evidence that 3-nitrotyrosine groups ionize between the pH values 6.2 and 8.3. The consequent difference in net negative charge of the wool proteins at these pH values could result in the differences in rate of contraction observed experimentally [3].

Kinetics of contraction of nitrated and HCl-treated fibers at pH 6.2. It must also be decided whether the kinetics of the second stage contraction in nitrated and HCl-treated fibers at pH 6.2 differ as a result of stabilization of the original structure by nitration or because the proteins of nitrated fibers have undergone greater configurational changes. Feughelman, Griffith, and Haly [9, 10, 11] have observed that the contraction of untreated wool fibers in 8 *M* LiBr at a pH of about 5 takes place in two stages, the second stage being retarded by iodination of the fibers by the method of Richards and Speakman [25]. They suggest that tyrosine is involved in strong polar bonds which must be broken to permit the second stage of contraction. The similarity between the levels of the first and second stages of contraction which they observed and the levels of the two stages for nitrated wool (Figures 6, 7, and 8) suggests that the effects of iodination and nitration have a common basis. Nitro and iodo groups are both electrophilic and on substitution in phenol cause an increase in positivity of the hydrogen atom in the hydroxy group [24]. This could increase the strength of hydrogen bonds in which it functions as donor, such as those with ionized carboxyl groups [14]. On this basis, differences in the kinetics of contraction of HCl-treated and nitrated fibers could be due to increased stability of the original structure.

However, Figures 6 and 7 show that wool fibers treated with HNO_3 at 20° C. for 1 hr., at 10° C. for 4 hr., or at 0° C. for 18 hr., resulting in the nitration of 29, 0, and 19% of the tyrosine respectively, show the typical two-stage contraction kinetics. Furthermore, pretreatments with HNO_3 at 10° C. for 8 hr. or at 20° C. for 1 hr. have almost identical effects on the contraction kinetics, yet the former treatment reduced the tyrosine content by 78% and the latter by only 29%. These facts are not in accord with the hypothesis that strengthening of the hydrogen bonds of tyrosine accounts for the slow second stage of contraction at pH 6.2. There is an additional difficulty. The titration curves (Figure 13) indicate that the pK_a of the nitrated tyrosine residues lies near 7. Such a value would be predicted for the 3-nitrotyrosine residues if they are not involved in hydrogen bond formation. In order to ionize hydrogen-bonded tyrosine residues in a protein structure, a pH of more than 12 is required [27], although the pK_a of the phenolic group of tyrosine is near 10.4; on this basis, if the 3-

nitrotyrosine residues of nitrated wool were hydrogen bonded, a pK_a in excess of 8.4 would be expected. The experimental evidence, therefore, does not support the view that the effects of nitration result from a strengthening of hydrogen bonds involving tyrosine.

The alternative possibility, that treatment with HNO_3 causes greater configurational changes in the wool proteins than treatment with HCl and that the new configuration is more thermostable than the old, appears to have more merit. By analogy with the facilitation of set by reduction of disulfide bonds [6], it might be anticipated that oxidation of disulfide by HNO_3 would also facilitate configurational changes. In favor of this hypothesis we may adduce the following facts. Trypsin digestibility is increased and the urea/bisulfite solubility is decreased more by HNO_3 than by HCl. The kinetic curve for wool treated with HNO_3 for 4 hr. at 10° C. shows the typical acceleration of the first stage and retardation of the second stage of contraction (Figure 6), although no measurable decrease in tyrosine content had occurred (Table II). Similarly, fibers treated with HCl for 4 hr. at 30° C. show the two stage effect when contracted in 5 *M* LiBr at pH 6.2 (Figure 12). In both cases the urea/bisulfite solubility was modified, and in the latter case trypsin digestibility was increased. The low trypsin digestibility of the wool treated at 10° C. for 4 hr. suggests that the configurational change does not necessarily involve extensive disordering of the wool proteins. The above observations also discount the possibility that steric effects of nitration are responsible for retardation of the second stage of supercontraction (*cf.* [29]).

Treatment with HNO_3 may also retard contraction by the oxidation of —SH groups (Table I). Interchange reactions between —SH and —SS— groups would be greatly reduced by these modifications. There is some evidence that such interchange reactions occur during supercontraction in solutions of LiBr [5].

The opposite effects of acid treatment on first and second stages of contraction. Whatever the hypothesis used to explain the effects of acid treatment on the kinetics of contraction of wool fibers, it must be concluded that the structure which is responsible for the first stage contraction differs greatly, chemically or physically, from that contracting in the second stage. In terms of our conclusion that configurational changes play a major part in modifying the contraction behavior of acid-treated fibers, it seems that the structure contracting in the second stage readily undergoes rearrangement to a form having a lower free energy. Since the first stage of contraction is not retarded by acid treatment, we may conclude that the composition of the structure responsible for this stage of contraction is such that either a similar modification does not greatly reduce the free energy of the system or the change to this new arrangement involves a large energy of activation. The reduction in the level of the equilibrium contraction for HCl-treated fibers in 4 *M* LiBr at pH 8.4 below that for the first stage of contraction would suggest that the latter explanation is more probable.

With such a model, the first stage of contraction would occur at normal rates, followed by a slow second-stage contraction. However, treatment with both acids causes the rupture of covalent bonds, and this would be expected to facilitate the contraction in both stages. Superposition of this effect on the above system could result in contraction to the first stage at increased rates, followed by a retarded second-stage contraction. Continuation of the process of breaking covalent bonds after the second-stage structure had reached its state of maximum thermostability would lead to an increase in the apparent level of the first stage, such as is apparent in Figures 8 and 9. Rupture of covalent bonds is probably responsible also for the elongation which follows the initial contraction of fibers treated in acid for prolonged periods at 30° C. (Figure 11). Elongation following contraction has been attributed to slippage between the contractile units of the wool [4], an effect which would precede solution of the wool proteins. Partial solution of the acid-treated fibers did in fact occur during supercontraction at pH 8.4.

The experimental data are equally well explained on the assumption that the structures responsible for first and second stages of contraction both undergo configurational change with consequent retardation of contraction but that the acceleration in contraction due to the rupture of peptide and disulfide bonds is greater with the first than with the second structure. The magnitude of this effect is apparent from Figure 12.

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The Relation of Wet and Dry Crease Recovery to Wash-Wear Behavior[1]

Richard Steele

Textile Research Laboratory, Rohm and Haas Co., Philadelphia 37, Pa.

Abstract

The chemical changes in cellulose fiber which lead to various wet: dry crease recovery ratios are reviewed. Covalent cross-linking of a dry fiber enhances both wet and dry recovery, and the ratio of the two values is believed to depend on the relative accessibilities of the fiber to water and to the cross-linking reagent. Water-sensitive links between cellulose chains can give high dry and low wet crease recovery. Cross-linking reactions carried out when the fiber is wet and swollen lead to a higher degree of intrachain reaction, which is equivalent to substitution, and to some interchain cross links. The swelling of such a fiber in water leads to good wet crease recovery, although the dry recovery is not improved.

To achieve good tumble-dry wash-wear behavior, both wet and dry crease recovery must be increased. In line- and drip-drying, the wet crease recovery has more significance than the dry.

THE original finishes for wash-wear cotton fabrics were simply more intensive applications of customary crease-resistant finishes, so that it was natural to consider immediately the possibility that wash-wear performance was related to dry crease recovery. Lippert, in one of the earliest papers on wash-wear cotton fabrics [9], dealt briefly with this relationship and pointed out how fabric construction factors and mechanical treatment during finishing could lead to situations where it apparently broke down completely. Lippert also reported a few wet crease recovery measurements and recognized that the relationship between wet and dry measurements could be important. In another early paper, Scott [16] came to the conclusion that crease recovery could not always be used for predicting wash-wear behavior and suggested that a high dry crease recovery might be a sufficient but not necessary condition for wash-wear behavior. Williams [23] also examined the relationship between wet and dry crease recovery of cotton fabric treated with dimethylolethyleneurea and a melamine resin and found that it was linear. He concluded that the same mechanism of recovery was operative in both the wet and dry states and that the dry recovery was as good a measure of ability to recover when wet as a wet measurement was. In a more recent paper [24], he states that for white cotton fabric treated with a variety of resins, wash-wear behavior is directly related to the wrinkle recovery and that wrinkle recovery may be used as an objective method for evaluating wash-wear performance. However, he limits this to cotton fabrics in a normal construction because the wet: dry wrinkle recovery relationship for cotton is different from that for synthetic fibers. Lawrence and Phillips [8] in their study of this problem found that crease recovery alone could not be relied upon to give adequate wash-wear rating. Although there seemed to be a relationship between the two properties, the range of crease recoveries found for a given wash-wear rating was so wide in their work that it would appear to be useless as a guide in evaluating wash-wear performance.

From the beginning, wet crease recovery seems to have been of interest. Lippert [9] and Williams [23] both reported wet measurements and both recognized that the wet: dry relationship might be significant in wash-wear behavior. Wet crease recovery can be measured by simply using the Monsanto procedure on samples which have been wet out with water, and this procedure has been used by Lippert, Williams, and others. However, a number

[1] This is part of a paper presented at the Gordon Research Conference on Textiles on July 14, 1959 at New London, N. H.

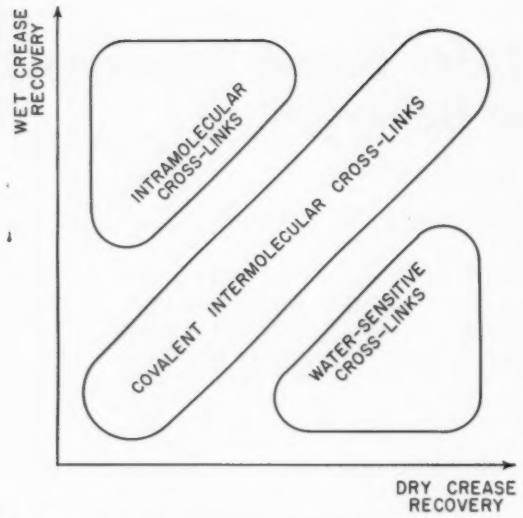

Fig. 1. Wet : dry crease recovery relationship for cellulose fabrics cross-linked in various ways.

of other methods have been described [6, 11, 22], and the wet crease recovery data in this paper were also obtained by a different technique, which has been described earlier [18]. In this method the standard creasing program is carried out under water, and the standard recovery period is allowed after the samples have been transferred to a dish containing a 1-in. layer of water over a mercury surface. At the end of the recovery, the angle is read by lining the sample up between a protractor on the top of the dish and its reflection in the mercury surface. This mercury flotation technique was used some years ago for measuring dry samples [3].

In this paper, we would like to consider in more detail the wet : dry crease recovery relationship and its significance in wash-wear behavior and to present some ideas about how these factors are related to chemically produced changes in the structure of the fibers. (By dry crease recovery we mean that measured at the normal conditions; 65% RH and 70° F.) For discussion, the wet : dry recovery relationship will be divided roughly into three areas which are shown schematically in Figure 1. There is the diagonal area where wet and dry crease recoveries are proportionately increased, the upper left corner where wet recovery is high and dry low, and the lower right corner where the reverse is true.

The central region of increasing wet and dry crease recovery seems to be accessible with cotton fabrics through treatment with relatively efficient intermolecular cross-linking reagents. This is demonstrated by the data of Williams [23, 24] on fabrics treated with dimethylolethyleneurea and methylolmelamine. The wet : dry crease recovery ratio of his treated cotton fabrics was approximately 0.9, and this figure has been confirmed by results in this laboratory.

The mechanism through which crease recovery is effected in this region is that which has been discussed in many papers on resin finishing. Crease recovery is enhanced by reduction of interchain slippage, and this is most effectively brought about by forming covalent bonds between chains. Dimethylolethyleneurea and methylolmelamine applied under the usual conditions are relatively efficient in the latter respect, forming a high proportion of intermolecular cross links with regard to other possibilities such as intramolecular cross-linking, side-chain grafting, and polymer deposition. Intermolecular cross-linking is effective in either the wet or dry state, but the ratio of wet crease recovery to dry depends on the relative accessibilities of the fiber to water and to resin. If all of the regions accessible to water can be penetrated and cross-linked by the resin precondensate, then the wet : dry ratio will be close to unity. If water can enter and swell regions of the fiber that are inaccessible to the cross-linking agent, the ratio will be less than one. In a cotton fiber, the region accessible to water on a molecular basis is small and its state of order is such that resin is able to enter it and to cross-link it relatively completely. The part of the cross-linked fiber that is swellable by water is very small compared to the cross-linked and highly ordered regions which are essentially nonswellable. In this case the wet and dry properties of the fabric are very similar and the wet : dry crease recovery ratio will be near one. In rayon, on the other hand, the accessible region is larger, the transition from amorphous to ordered portions is more gradual, and even when the resin-permeable area of the fiber is cross-linked, there is still an extensive area which is water-swellable. The effect of this water swelling is to disrupt polar interchain forces, which permits greater chain slippage in the wet fiber and gives lower crease recovery. The wet : dry crease recovery ratio of ordinary viscose cross-linked with dimethylolethyleneurea is in the range of 0.55 to 0.75, substantially lower than the ratio for cotton. This difference is not due just to the difference in cross link concentration in the accessible regions, since it persists to high resin load-

ings. If it is due to a difference in the distribution of order in cotton and rayon, then one might expect to find that the wet : dry ratio might be different for rayons of different structure than ordinary viscose. There are several cases where this is true. For example, challis fabrics made from Super L and Fabelta Z-54 rayons have wet : dry ratios between those of cotton and ordinary viscose. Some data for Fabelta Z-54 are shown in Figure 7. Both of these fibers are reported to have all-core structures.

The origin of differences in wet : dry crease recovery ratio may be clarified by reference to Marchessault and Howsmon's estimate of the lateral-order distribution in cellulose fibers [10], part of which is shown in Figure 2. The distribution curves are shown for cotton, conventional viscose rayon, and for a high-strength, low-elongation modified viscose such as Z-54. It is postulated that a given cross-linking reagent can penetrate each of the fibers up to a certain level of order which is somewhat less than the penetration of water alone. The area under each distribution curve between these two limits represents the portion of the fiber which is water-swellable but not cross-linked by the reagent. The water sensitivity of its mechanical properties, including crease recovery, will depend on the ratio of this area to the total area under the curve.

In the lower right hand corner of the map in Figure 1, dry crease recovery is increased with little or no enhancement of the wet behavior. There are several ways to produce fabrics whose crease recoveries fall within this region. In general, they are all variations of the principle of introducing water-sensitive cross links which are broken and ineffective during the wet measurement. The simplest way to do this is to dry the fabric thoroughly so that the polar interchain forces, such as hydrogen bonds, are more highly developed. Aminoplast resins which are not efficient cross-linkers, such as low formaldehyde content urea-formaldehyde precondensates (monomethylolurea, for example) tend to give results which fall in this region. We have found this to be particularly true with rayon, as shown later, but it also tends to occur with cotton, as in the data given by Williams [23].

The upper left hand corner of Figure 1, where wet recovery is much higher than the dry, is an area which has been neglected until recently, but it presents some interesting problems. First of all, results in this area can be obtained by cross-linking the fabrics, but the cross-linking must be done in the swollen state. This gives very different effects from dry cross-linking and will be discussed in detail later.

Two other methods for getting results in this region on cellulose fibers are by applications of lightly condensed urea-formaldehyde precondensates and by normal resin treatment of rayon which has been pretreated with strong caustic. An example of the first technique is the effect of Rhonite [2] 313 on the crease recovery of rayon challis, as shown in Figure 3. The decrease in dry crease recovery ordinarily shown by surface resins is apparent, but the wet recovery rises strikingly. This resin precondensate is partly diffusible into the fibers [7], but the portion deposited as surface resin is probably responsible for the effects observed. The surface resin spot welds fibers together inside the yarns and produces a stiffened three-dimensional structure. The resin links are essentially inextensible, so that when the dry fabric is deformed their macroscopic cross-linking effect reduces the possibilities for stress distribution, leading to higher localized stresses in the strained region. The nonrecoverable strain produced in these areas accounts for the poorer dry crease recovery. In the wet state, the fiber modulus is so reduced by swelling that satisfactory stress redistribution can occur by extension of the fiber segments between resin bonds, while the elastic re-

[2] Rhonite is a trademark of the Rohm and Haas Co.

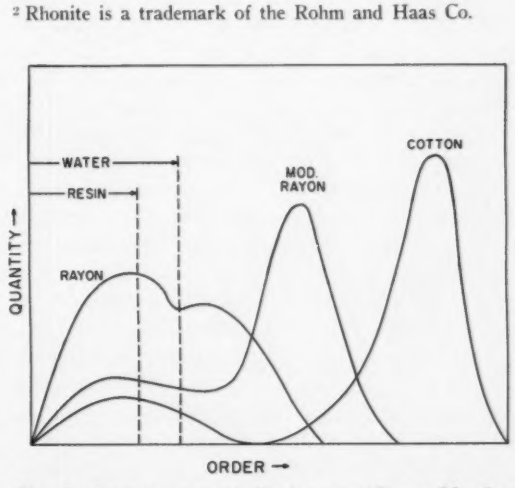

Fig. 2. Lateral order distribution according to Marchessault and Howsmon [10] for cotton, ordinary viscose, and a high-strength, low-elongation viscose, with postulated qualitative limits for accessibility of water and resin.

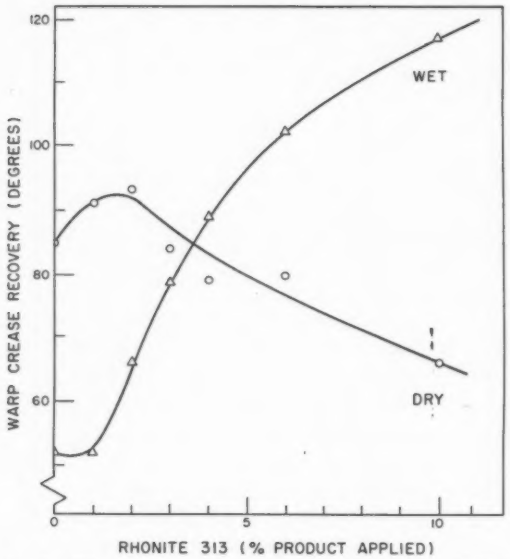

Fig. 3. Effect of a partially condensed urea-formaldehyde resin on the crease recovery of rayon challis.

covery of the whole structure has been sufficiently enhanced by the resin bonding to give better wet crease recovery.

The second method mentioned has been studied by Wannow [21], who was following a procedure proposed in patents issued to Marsh and Hunt [11a]. If rayon is swollen in aqueous sodium hydroxide and washed, but not dried, before being impregnated and reacted with resin in the usual dry-cure way, the wet crease recovery of the treated fabric goes up with increasing caustic concentration while the dry value comes down. Data from an experiment of this type are shown in Figure 4. Rayon challis was impregnated with sodium hydroxide solutions of various concentration. One minute after impregnation the samples were neutralized in dilute acetic acid and thoroughly washed. They were then squeezed out by hand and transferred to a large excess of resin solution containing 5% solids of urea-formaldehyde paste resin and 5% solids of dimethylolethyleneurea. Ammonium chloride was used as a catalyst at a level of 0.2 mmole/g. of precondensate. After being steeped in this resin solution for 30 min., the samples were padded, framed, and cured for 10 min. at 150° C. without predrying. The dry crease recovery goes down with increasing caustic concentration while the wet recovery goes up. This effect is believed to result from cross-linking the swollen, disordered structure produced by the caustic pretreatment. This is basically the same mechanism involved in wet cross-linking.

A number of reactions have been proposed for cross-linking cellulose in a wet and swollen condition. The following may be cited as examples. Morton [13] heated rayon samples in 40% formaldehyde with sulfuric acid as a catalyst and obtained a cross-linked product with properties quite different from those of rayon cross-linked in the dry state. Schoene and Chambers [15] cross-linked cellulose in aqueous solutions of divinyl sulfone, using alkaline catalysis. Brown and Steger [2] formed ether cross links in cellulose fabrics by impregnating with 1,3-dichloropropanol-2 and then treating them with hot solutions containing sodium hydroxide and sodium chloride. The principal advantage claimed for these processes has been dimensional stabilization, although Morton stressed the fact that water imbibition and swelling were increased. Dry crease recovery is not significantly improved. Cross-linking in the swollen state actually goes back to the work of Eschalier [5] on the treatment of regenerated cellulose with formaldehyde. It seems very likely that some of the processes he suggested led to such results, and an increase in moisture regain is claimed as a result of

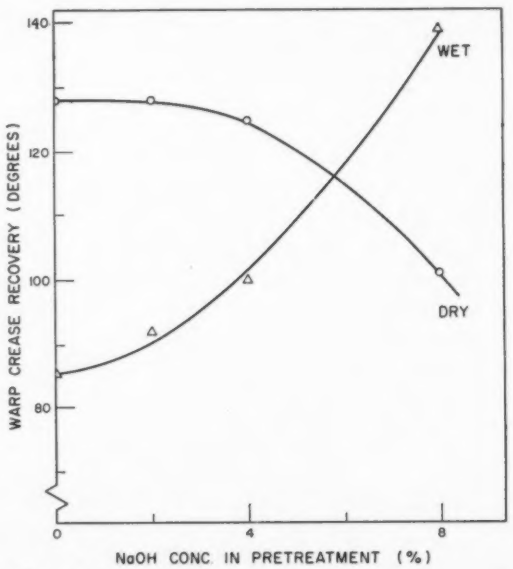

Fig. 4. Effect of caustic pretreatment on the crease recovery of rayon challis treated with a mixture containing 5% urea-formaldehyde paste resin and 5% dimethylolethyleneurea.

his treatment. The effect of the water content of the system on the reaction of formaldehyde with cellulose was also studied in 1931 by Wood [25], who showed that quite different products could be obtained at different moisture levels.

Cellulose cross-linked wet by processes such as those cited has some very different properties from that reacted in the dry state. Specifically, it is different in that it has high moisture regain, high swelling in water, and low dry crease recovery. The materials cross-linked in the swollen and the condensed state are alike in having high wet crease recovery and in being insoluble in cuprammonium hydroxide solution. The two major points to be resolved revolve around the reversed sorption and swelling behavior and the low dry crease recovery.

Walker [20], discussing Morton's patent, suggested that the hydrophilic nature of the product resulted from a swelling action of the treating solution which was made permanent by a minimal amount of cross-linking. Added to this must also be the well-known effect of substitution along the cellulose chains, which can produce high swelling or solubility even when the substituent is not hydrophilic but is, for example, a methyl or ethyl group.

When polymers are cross-linked in the swollen state, the proportion of intramolecular to intermolecular cross links is probably much higher. This seems intuitively reasonable, since swelling separates the chains and reduces the probability that two will be close enough to be bridged by the cross-linking reagent. It is also suggested by the work of Minnema and Staverman [12], who studied the copolymerization of methyl methacrylate and a dimethacrylate which could act as a cross link. The ratio of intra- to intermolecular reaction of the dimethacrylate was found to be strongly dependent on the dilution of the polymerizing system.

Celluloses which are cross-linked wet are insoluble in cuprammonium hydroxide solution, indicating that some intermolecular cross-linking has occurred. The most likely sites for this would appear to be in the fringes of the crystalline regions, where the chains are drawn closer together. This results in a different distribution of the intermolecular cross links from that in fibers which have been cross-linked in the dry, condensed state, where a more random distribution in the accessible region might be expected.

A combination of substitution and moderate peripheral cross-linking in the accessible region would be expected to result in a fiber with considerable swellability whose swollen structure is stabilized by the constraint of the cross links. Such enhancement of swelling is postulated as a second basic mechanism for moving about the wet : dry crease recovery map in Figure 1. It permits moving in the vertical direction only, but by suitable combinations with dry cross-linking techniques the area in the upper left-hand corner of the diagram is generally available. It seems reasonable to believe that when a wet fiber is deformed by bending there would be a region in the strained area which would be forced to deswell. This is suggested by the work of Treloar [19] and others [14, 17] on the effect of deformation and constraint on fiber swelling. Then the tendency of the fiber to reabsorb water when the deforming force is removed would provide a driving force tending to restore the original unstrained form of the fiber. If the tendency of the fiber to swell is increased by the finishing treatment, the available driving force for recovery from wet creasing would also be increased. This means, among other things, that the wet crease recovery of cellulose fabrics should be higher in solutions which swell them more strongly than water. This has been confirmed for viscose challis in various swelling solutions by Dr. R. A. Gill of this laboratory, who obtained the results in Table I.

TABLE I. Crease Recovery of Viscose Challis in Various Swelling Media

Medium	Swelling time, hr.	Crease recovery, warp, °
Water	—	49
6 *M* LiCl	0.8	56
	2.5	92
11 *M* LiCl	0.8	85
	18.0	97
1.5 *M* NaOH	0.5	106

The important points of the discussion of Figure 1 may be summarized as follows.

1. To move to the right on this crease recovery map, toward higher dry crease recovery, molecular slippage in the cellulose fiber must be reduced. This can be done by drying it, for example, or grafting on polymer side chains, but the most effective way is to tie chains together with covalent cross links, carrying out the reaction in the dry, condensed state.

In the latter case, and whenever the effect is not sensitive to water, wet as well as dry crease recovery will be enhanced. If there is a low proportion of the fiber which is accessible to water and inaccessible to the cross-linking reagent, the wet : dry crease recovery ratio will be near unity. However, if there is a significant region accessible to water which is not cross-linked, the ratio will be less.

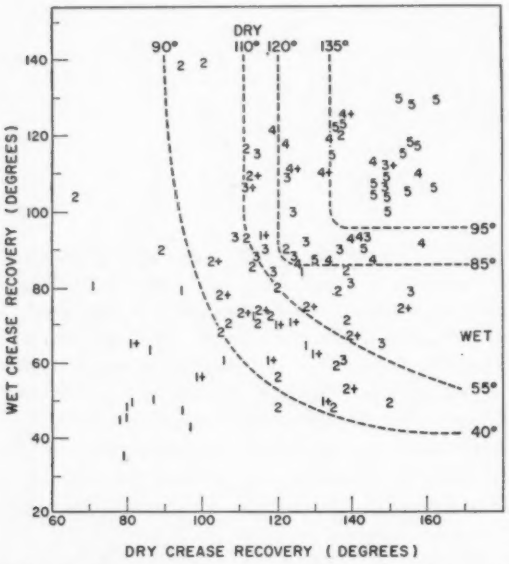

Fig. 5. Crease recovery map for viscose fabrics with various finishes. The number plotted is the tumble-dry wash-wear rating.

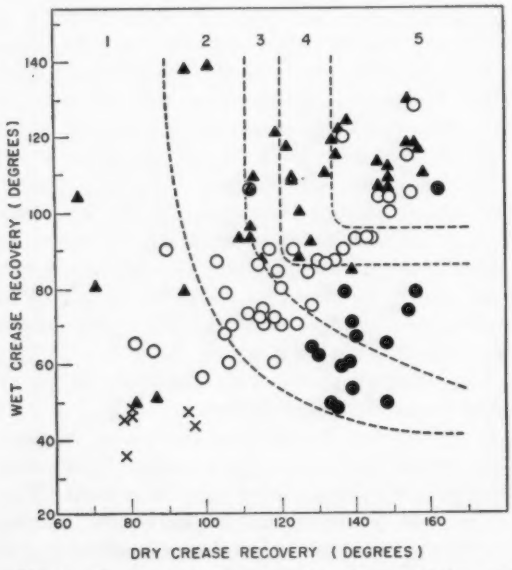

Fig. 6. Crease recovery map for viscose fabrics with various finishes. Same data as in Figure 5, but identified by class of treatment. See text for identification.

2. Efficient covalent cross-linking reagents produce wet : dry crease recoveries along a diagonal line with a positive slope which depends on the accessibility of the cellulose fiber to resin and to water, as just explained.

3. To move up on the chart and obtain higher wet crease recovery is possible by stabilizing the wet swollen configuration of the fabric. This can be carried out by cross-linking the fiber in the swollen state, which results in a higher proportion of intramolecular cross-linking, i.e., double-ended substitution, which enhances the swellability. This enhanced swellability produces a driving force when the fabric is put in water which helps attainment of the stabilized, swollen, cross-linked condition, and thereby gives higher wet crease recovery.

4. Cross links or side chains which are broken or removed by water may produce fabrics with high dry crease recovery and little or no enhancement of wet crease recovery.

Wash-Wear Behavior

The wash-wear behavior of cellulosic fabrics is affected by other factors than those which are measured by crease recovery. Fabric construction, color, and pattern are undoubtedly important, as well as the type of washing and drying procedures used. However important these may be, there are two principal first-order effects which are related to the chemical finishing the fabric receives. One is the nature of the treatment which leads to changes in wet and dry crease recovery, and the second is the drying method employed in the washing procedure. The wash-wear data discussed below were obtained by the tentative AATCC method [1] using a 10-min. 140° F. wash and, in most cases, tumble drying. The Monsanto plastic models were used as standards.

Figure 5 is a crease recovery map made with data from a variety of treated rayon samples. There are approximately 100 points, and about 80 of them are laboratory treatments on a 3.5-oz. rayon challis. The remainder are also laboratory finishes on a butcher linen and a gabardine. The tumble-dry wash-wear rating has been plotted against wet and dry crease recovery, and then boundaries have been drawn which delineate the areas where various wash-

wear levels occur, rather in the manner of a topographic map. The numbers in the margins indicate the minimum dry and wet crease recoveries required for descending wash-wear ratings, beginning in the upper right-hand corner. They should not be taken as absolute figures since they can be influenced by the other factors mentioned earlier. However, it is reasonable to conclude that both wet and dry crease recovery must be improved to give tumble-dry wash-wear behavior to rayon fabrics.

Figure 6 is a key to the treatments involved in Figure 5. Both figures have the same points on them, but in Figure 6 they are coded by treatment. The crosses at lower left are untreated fabric run as controls in the several series of experiments. The solid black circles are applications of urea-formaldehyde precondensates of varying formaldehyde : urea ratio. The lower points in this group are from samples treated with monomethylolurea, and the wet : dry crease recovery ratio rises with the formaldehyde content. The highest filled circle shown, in the "5" wash-wear region, is from dimethylolurea. Urea-formaldehyde condensates of low formaldehyde : urea ratio are not efficient cross-linkers, and while the grafted side chains from monomethylolurea may be effective to some degree in inhibiting chain movement in the dry state, they are less effective in the wet swollen state, contributing little to wet crease recovery. Treatments with these materials therefore fall in the lower right-hand corner of the map with low wet : dry crease recovery ratios. The open circles scattered along the diagonal of the chart are from samples treated with dimethylolethyleneurea reacted in the dry state, which results in an efficient intermolecular cross-linking.

The black triangles are all combinations of various levels of Rhonite 313 and dimethylolethyleneurea, except for the two points near the ordinate scale and the two directly under the "2" wash-wear rating label. The former are treated with Rhonite 313 alone, while the latter are caustic pretreatments followed by a mixture of dimethylolethyleneurea and a urea-formaldehyde paste resin as described above. The relatively high wet : dry crease recovery ratio of these samples has been of little value in attaining good tumble-dry wash-wear ratings.

Figure 7 combines some cotton and rayon data to demonstrate the relationship between the two fibers. The data in the circles are from cotton muslin and printcloth, and those not outlined are from viscose rayon challis and butcher linen; all fabrics have been treated with increasing levels of dimethylolethyleneurea. The data for the two fibers fall along separate lines of different slope, but the construction differences between each pair of fabrics are not significant. It should be noted that the dry crease recovery limits here are lower than in Figure 6 due to the influence of the cotton, but the wet limits are about the same. The data in squares are from a challis made from Fabelta Z-54, and fall between the lines for cotton and ordinary viscose.

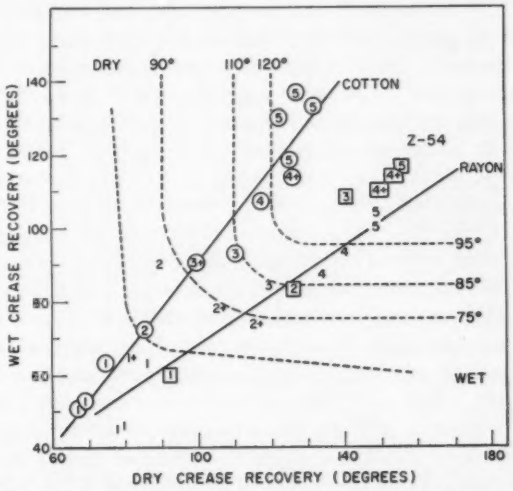

Fig. 7. Crease recovery map comparing some cotton and rayon fabrics.

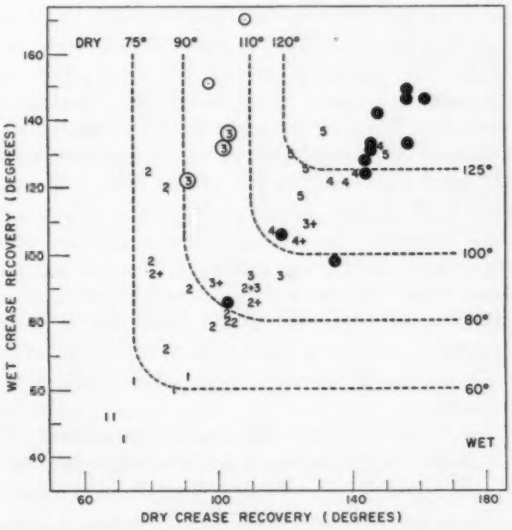

Fig. 8. Crease recovery map for cotton printcloth. See text for identification of points.

TABLE II. Minimum Crease Recovery Required for Various Levels of Wash-Wear Performance

Wash-wear rating	Cotton		Rayon	
	Dry	Wet	Dry	Wet
5	120	125	135	95
4	110	100	120	85
3	90	80	110	55
2	75	60	90	40

Figure 8 shows data for cotton printcloth. The "1's" in the lower left are untreated, and the wash-wear ratings and filled circles scattered along the diagonal again represent dimethylolethyleneurea treatments. The three uppermost "2's" in the "2" region are from fabrics reported to have been treated with a commercial process known as the Belfast[3] treatment. The "2+" rating at 81° dry recovery and 95° wet is from a sample treated only with 10% Rhonite 313. The encircled points are for samples treated with an experimental cross-linking compound which combines wet and dry reaction. The point at 151° wet crease recovery and 98° dry is for a sample that has been cross-linked with formaldehyde in aqueous solution according to the process of Morton [13]. The very high wet crease recovery, 170°, of the point at 109° dry recovery is for printcloth cross-linked in an alkaline aqueous solution of divinyl sulfone according to Example 4 of the patent of Schoene and Chambers [15].

For cotton, as with rayon, it appears that both wet and dry crease recovery enhancement is necessary to move into regions of good tumble-dry wash-wear behavior. It should be emphasized again that the minimum recoveries noted along the topological boundaries should not be regarded as absolute values. However, an examination of dry crease recovery and wash-wear data on 50 fabrics treated in mill trials with various triazone and other aminoplast resins indicates that the dry limits correlate well with our company's experience. If the wet and dry limits from Figures 5 and 8 are compared, it is rather striking that the cotton limits for a given wash-wear rating are close to each other and close to the average of the rayon limits. This is shown by Table II.

The relation of wet and dry crease recovery to tumble-dry wash-wear behavior which has been developed above is schematically summarized in Figure 9. Tumble-dry wash-wear behavior is related to wet and dry crease recovery and both must be enhanced to improve tumble-dry wash-wear rating. Covalent intermolecular cross-linking reagents are the most effective way we know for achieving this in both cotton and rayon, and they act by reducing molecular slippage in the fiber. For drip-drying and line-drying the pattern is rather different, and in both cases the ratings seem to show a much stronger dependence on wet crease recovery than on dry. Figure 10 shows the relation between line- and tumble-dry wash-wear ratings for the two cotton and two rayon fabrics described earlier which were treated with increasing levels of dimethylolethyleneurea. The slope of the cotton curve is much steeper than for rayon, reflecting the higher wet : dry crease recovery relationship shown in Figure 7. It should be expected that wet crease recovery would be most important in drip drying, and on the basis of rather limited data, it is suggested that the crease recovery : wash-wear map for this case might be something like Figure 11. In this case it is obvious that we can get to regions of good wash-wear characteristics not only by dry covalent cross-linking but by wet-state cross-linkage, which increases the tendency of the fiber to swell and lightly cross-links the swollen structure.

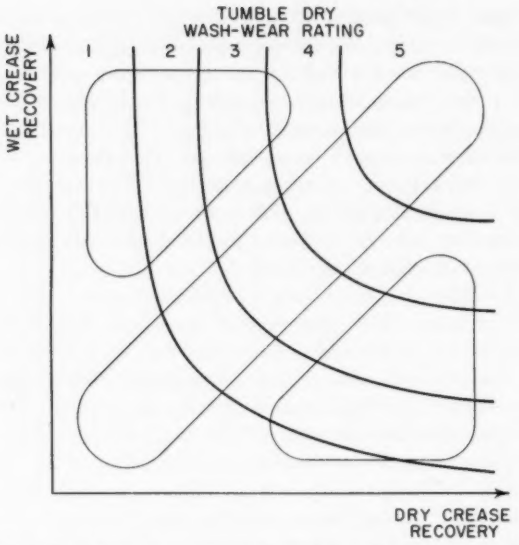

Fig. 9. Schematic representation of the relationship of wet and dry crease recovery to tumble-dry wash-wear behavior.

Earlier this year Cooke [4] published some wet

[3] Belfast is a trademark of the Deering Millikin Research Corp.

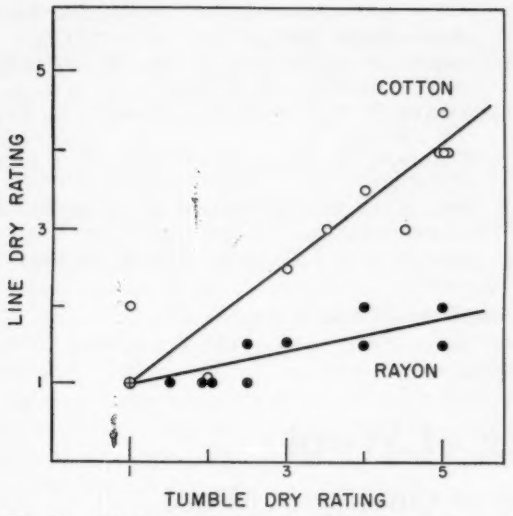

Fig. 10. Relation of line-dry to tumble-dry wash-wear ratings for cotton and rayon fabrics.

and dry crease recovery data on samples which had been ranked in wash-wear behavior after both drip- and tumble-drying. These confirmed, to a limited extent, the greater significance of wet crease recovery in the drip-drying procedure, but again a limited amount of data was available.

Conclusions

Wet and dry crease recovery tests are measures of changes in fabric properties which are of major importance in determining wash-wear behavior. The relationship between crease recovery and wash-wear rating depends on the drying procedure used in wash testing. For tumble-drying, both wet and dry crease recovery must be increased to achieve good wash-wear performance on cotton and rayon. In line or drip drying, wet crease recovery is a more significant factor than dry.

Concurrent increases in wet and dry recovery can be obtained by finishing agents which reduce interchain slippage, and the most effective agents are those which form covalent cross links between the cellulose chains. Cross-linking reagents applied to fabrics which are in the wet, swollen state yield a larger proportion of intramolecular reaction than the usual dry-state application. Wet cross-linked fabrics tend to be stabilized in the swollen state, so that moisture regain and swellability are enhanced. The latter property is largely responsible for their high wet crease recovery properties.

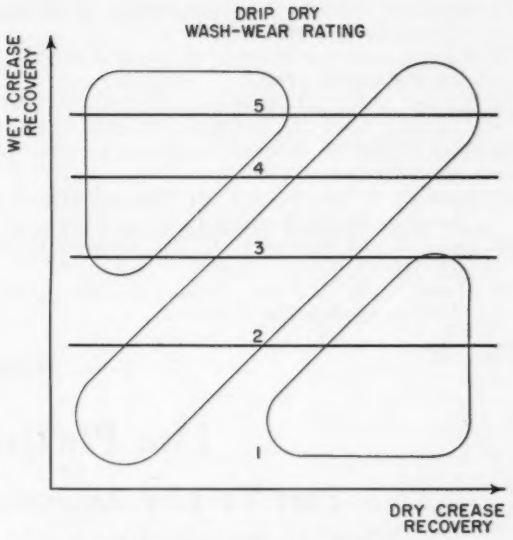

Fig. 11. Schematic representation of the relationship of wet and dry crease recovery to drip-dry wash-wear behavior.

Acknowledgment

Discussion with Dr. John L. Gardon has been of considerable help in formulating some of the ideas in this paper.

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The Plasticity of Wool

Part V: The Assessment of Quality in Wool

K. J. Whiteley and J. B. Speakman

Department of Textile Industries, Leeds University, England

Abstract

Differences of substance among various wools play an important part in determining their suitability for use in manufacturing different types of fabric, and quality in wool cannot be assessed by measuring only the dimensional characteristics of the fibers.

Introduction

In some countries, particularly those without long experience in selecting and using wools, there is a growing tendency to assume that the quality of a wool may be assessed by measuring the dimensional characteristics of the fibers, i.e., fineness, crimp, and length, due attention being paid to the uniformity of the fibers in these respects. Special importance is attached to the fineness of the fibers, and a number of instruments have been developed for the rapid measurement of the average fiber diameter of samples of wool. While such measurements have their uses, it does not seem to be realized that any attempt to assign fiber diameters to quality numbers must be based on one or other of the following assumptions: either the substance of which the fibers are made is immaterial or the substance of all wools is the same. If the first assumption were true, it would be immaterial, as regards both the behavior during processing and the properties of the product, whether fibers were made of, say, nylon or wool, provided that both types of fiber are identical in fineness, crimp, and length; this is clearly absurd. The alternative, that the substance of all wools is the same, has already been shown to be invalid by measurements of plasticity [1]. In addition, some evidence has been advanced to show that differences of substance are detected by the wool classer [3], but it does not follow that they are important to the top-maker, spinner, and manufacturer. The purpose of this investigation was to discover whether the differences of substance which are revealed by plasticity measurements play any part in the assessment of quality by the wool buyer, as well as in his selection of the wools which are best suited to particular end uses.

Experimental

Selection and Purification of Wools

The wools chosen for examination were provided by different sections of the wool textile industry of Great Britain. Each sample was well authenticated as regards behavior during processing; details of the basis of selection are given later.

The wools were purified by extraction with ether in a Soxhlet apparatus, followed by repeated washing in cold ethanol and water. Only the intact root ends of the fibers were used.

Procedure

Plasticity measurements were carried out in the usual way [1, 3] by observing the rate of creep of single fibers under stress in distilled water at 22.2° C., and the plasticity constant k was evaluated as the slope of the straight line which is obtained by plotting log $(E - E_t)$ against t, where E_t is the percentage extension at time t (minutes) and E is an arbitrarily chosen limiting extension. A load of 6 kg./mm.^{2} was used; the values of plasticity are not, therefore, comparable with those of the previous paper in this series [3], which were obtained with a higher load.

Results

Wools with Similar Dimensions but Different Quality Numbers

During the course of his lecture on "Scientific Measurement in Commercial Practice" to the Bradford Textile Society, Mr. T. Hunter [2] exhibited two tops, one made from New Zealand wool and the other from South American (B.A.) wool. Without exception the trade experts had assessed the New Zealand top as a 50s and the B.A. top as a 46s. When, however, measurements of fiber diameter and length were carried out, the two tops were found to be remarkably alike, as is shown by the data of Table I. The data are based on 400 measurements of fiber diameter and 600 measurements of length.

It is obvious from these results that fibers of the same diameter do not necessarily have the same quality, and the wools were therefore examined to discover what factors, other than length and fineness of fiber, affect the judgment of the expert. In the case under consideration, it is possible that the greater, though small, amount of crimp in the New Zealand wool may have affected the assessment of quality, but the other possibility, that there are differences of substance which are detected by the expert, was examined by determinations of plasticity. The results are given in Table II, each value being the mean of 50 observations. There are clearly important differences of substance between the two wools, and it appears that the expert in these cases prefers the more plastic (the better handling) wool.

TABLE I. Dimensional Characteristics of New Zealand and B.A. Tops

Wool	Mean diameter, μ	CV, %	Mean length, cm.	CV, %
N.Z. 50s	34.9	25.8	14.8	23.8
B.A. 46s	33.3	27.5	16.4	32.4

TABLE II. Plasticities of New Zealand and B.A. Wools

Load = 6 kg./mm^2. E = 70%

Wool	Mean diameter of tested fibers, μ	Plasticity (k), arbitrary units	CV of plasticity, %
N.Z. 50s	38.0	30.0	46.7
B.A. 46s	38.7	15.2	34.8

TABLE III. The Plasticity of Lamb's Wools

Load = 6 kg./mm^2. E = 80%

Wool	No. of fibers tested	Mean diameter of tested fibers, μ	Plasticity (k), arbitrary units	CV of plasticity, %
Carin	16	22.8	78.6	72.7
Pindabunna	15	22.6	27.1	38.7

Selection of Wools for Blending with Cashmere

By itself alone the case of the two tops is, of course, insufficient to establish whether the expert does detect differences in the substance of different wools. Through the kindness of Mr. K. G. Ponting, a woolen manufacturer in the West of England, two samples of lamb's wool were next brought to our attention. About one of these (Carin; Victoria) he inquired why it should command such a fabulous price—double that of any other wool. He was unable to explain why the price of another lamb's wool (Pindabunna; Western Australia) should be so much lower, although he was aware that the Carin wool was bought for blending with cashmere. Diameter measurements (300 fibers) showed that the Carin wool was considerably finer (17.3μ) than the Pindabunna wool (20.6μ), but, in addition, it was found that the Carin wool was very much more plastic. The results are given in Table III.

Unfortunately, the difference in fineness of the wools in bulk makes it impossible to determine the extent to which differences of substance govern the preference for Carin wool, though the softness as-

TABLE IV. The Plasticities of Australian and Other Wools

Load = 6 kg./mm². $E = 80\%$

No. of sample	Type of wool	No. of fibers tested	Mean diameter (μ) of		Plasticity (k), arbitrary units	CV of plasticity, %
			Tested fibers	Bulk		
127	Lamb's wool; Victoria	15	23.1	23.4	53.6	24.9
10	Lamb's wool; Victoria	12	21.7	18.6	45.3	44.1
31	Lamb's wool; Kenya	4	20.3	20.8	43.5	13.6
52	Tasmanian (clothing)	3	18.3	16.6	37.8	30.6
58	Lamb's wool; Cape	12	15.5	15.4	37.6	23.3
64	Lamb's wool; Queensland	10	23.5	17.3	37.1	16.6
22	Queensland (weaners)	13	18.3	18.2	29.5	36.4
109	Western Australia (AA weaners)	6	19.8	17.8	21.9	17.3

TABLE V. Plasticity of Cashmere

Load = 6 kg./mm². $E = 80\%$

No. of fibers	Mean diameter, μ	Plasticity (k), arbitrary units	CV of plasticity, %
5	18.8	54.6	28.6

sociated with the high plasticity of the latter is, of course, a very desirable characteristic of any wool which is to be blended with cashmere.

Eight further samples of wool were, therefore, obtained from Mr. Ponting. Their characteristics, which were determined without knowledge of his opinion of the wools, are given in Table IV.

When these results were available it was disclosed that the two of highest plasticity—127 and 10—brought prices about three times those of the remaining wools, despite the fact that 127 is so much coarser than the others. Both wools were bought for blending with cashmere, and, of the two, 10 was regarded as the better, presumably because of combined fineness and high plasticity.

At this stage of the work it seemed desirable to determine the plasticity of cashmere itself. The sample examined had been graded First White China; the results are given in Table V. It seems probable, therefore, that the selection of the lamb's wools which are best suited for blending with cashmere is based on the need to match plasticity as well as other characteristics.

Selection of Wools for High-Class Woolen Overcoatings (Scotland)

The wools chosen for this section of the wool textile industry must be capable of giving an excellent handle to the final product, and in the light of the preceding results it seemed likely that the wools would be characterized by high plasticity. Two samples, typical of the types in general use, were examined, as well as a lamb's wool selected for blending with cashmere in overcoatings. The results are given in Table VI. As was expected, all the wools are remarkable for their high plasticity. In spite of the fact that the lamb's wool has the lowest plasticity of the three, it is preferred for blending with cashmere, because other factors, such as luster and fineness, as well as high plasticity, play their part in determining suitability.

Blending of Wools in Top-Making (Yorkshire)

Five samples of wool were supplied by a Bradford top maker. These included two pairs of samples, chosen to test the top maker's opinion that the fibers of Montevideo wool must be finer than those of Australian wool if comparable tops are to be obtained. The fifth wool (Concordia) had been found difficult to match because of its "inherent resilience and springiness." A summary of the results obtained with these wools is given in Table VII.

In agreement with the top maker's judgment, the South American wools are much lower in plasticity than the corresponding Australian wools; it is particularly interesting that the Concordia wool, which is a case of special difficulty, should have the lowest plasticity so far encountered.

Selection of Wools for the Manufacture of West of England Billiard Cloths

The preceding examples make it clear that wool should have a high plasticity in cases where excellence of handle is a primary requirement, and it is

TABLE VI. Plasticities of Wools for Overcoatings

Load = 6 kg./mm². E = 80%

Type of wool	No. of fibers tested	Mean diameter, μ	Plasticity (k), arbitrary units	CV of plasticity, %
Australian warp	7	26.8	70.4	33.7
Cape warp	6	22.8	62.5	24.8
Australian lamb's wool	8	20.7	46.7	14.0

TABLE VII. The Plasticities of Australian and South American Wools

Load = 6 kg./mm². E = 80%

Type of wool	No. of fibers	Mean diameter (μ) of		Plasticity (k), arbitrary units	CV of plasticity, %
		Tested fibers	Bulk		
Australian 64s	13	20.6	19.8	65.1	26.8
Montevideo 64s	11	27.1	24.9	33.3	22.6
Australian 58s	6	35.4	30.6	40.0	24.1
Montevideo 58s	8	40.4	37.4	19.5	18.3
Concordia 58s	8	29.6	27.1	13.5	15.0

obvious from first principles that wools of low plasticity will be preferred for some fabrics, e.g. pile fabrics, where resilience of the fibers is essential. Another use for which wools of high plasticity are unsuitable is in the manufacture of West of England face cloths, such as billiard cloths, where the finishing routine includes such heavy and prolonged milling that the cloth is reduced to half its original width. Three wools, A, B, and C, were supplied by a firm specializing in the manufacture of this type of fabric. Two of the wools, A and B, had been found to be satisfactory, A being preferred to B, while the third (C) belonged to the type which past experience had shown should never be used. All the wools had the same number of crimps per inch (20); the results of plasticity measurements are given in Table VIII. When the scaliness of the three wools was measured in air and water by the violin bow method [4], the results of Table IX were obtained. The wool (A) which is preferred for the manufacture of billiard cloth has the lowest scaliness in air and the highest under water. But since wool B, which is only a little less suitable than A, has almost exactly the same scaliness as the rejected wool (C) in water, it must be concluded that the high scaliness of A in water is not the factor which determines its special suitability for use in billiard cloths. The deciding factor may be deduced from the fact that wool C was rejected because it gave a felt which was loose and open instead of the required compact mass.

TABLE VIII. The Plasticity of Wools Used in the Manufacture of West of England Face Cloths

Load = 6 kg./mm². E = 80%

Wool	No. of fibers tested	Mean diameter of fibers tested, μ	Plasticity (k), arbitrary units	CV of plasticity, %
A	14	16.6	16.1	11.7
B	12	18.9	26.6	18.2
C	9	17.4	70.3	24.4

Such a result can be attributed to the high plasticity of the wool, which must make for impaired penetrating power of the root ends of the fibers. Further, if a low plasticity is desirable, the three wools are placed in the correct order of merit by plasticity measurements, with B only a little inferior to A.

Discussion

In the light of the preceding results there can be little doubt that the wool buyer, besides taking account of the dimensional characteristics of wools, is able to detect those differences of substance which play an important part in his recognition and choice of the wools which are best suited to particular end uses. Although the wools used in each section of the investigation were provided by a single buyer, it should not be assumed that the above attempts to find a physical basis for the preference for particular

TABLE IX. The Scaliness of Wools Used in the Manufacture of West of England Face Cloths

Wool	Scaliness, %	
	Air-dry	Under water
A	13.9	39.2
B	36.1	28.7
C	29.3	27.7

wools are based on the insecure foundation of a single person's judgment in each case. Different buyers had no difficulty in detecting the wools which were suitable for blending with cashmere and those which would withstand heavy milling, as is shown by their comments on the various samples (Table X).

It will be noticed that all the buyers were strongly biased in their estimation of fiber diameter by the crimpiness of the wools, but the consistency of their judgment of the special features of the different wools is remarkable. The exact manner in which they detect the differences of substance, of which so much use is made, has still to be determined, though it is clear that each buyer's judgment undergoes progressive refinement through the comments made by the user on the processing behavior of the wools supplied.

Acknowledgment

One of the authors (K. J. W.) is indebted to the International Wool Secretariat for financial assistance.

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TABLE X. Buyers' Reactions

Carin and Pindabunna Wools

Buyer 1. (submitted Carin and Pindabunna).

Carin: Soft, lustrous, typical of the district from which it came. Shows certain unique features, due to soil or environment and not related to physical dimensions, which make it suitable for blending with cashmere.

Pindabunna: Much better staple formation and finer than Carin. Suitable for woolen suitings but not for blending with cashmere.

Buyer 2. (submitted A, B, and C wools).

Carin: Had observed that this type always brought a high price; very soft. Had purchased a similar lot for blending with cashmere.

Pindabunna: Would be harsh to handle in bulk; this would outweigh its regularity and fineness.

Buyer 3. (submitted South American wools).

Carin: Too short for his purposes; did not use lamb's wools at all; considered it to be distinctly coarser than Pindabunna.

Pindabunna: Emphasized its good length and regular crimp; described it as a "foodier" wool better suited to his purposes.

A, B, and C Wools

Buyer 1. On being informed that the wools showed different felting properties, he immediately stated that A would be ideal for felting, because it could undergo severe physical treatment; it was very fine but very tough. B was similar to A but not so suitable and was coarser. C was recognized as being of the soft, lustrous type suitable for blending with cashmere, but was thought to be the coarsest of the three.

Buyer 2. Had submitted the three wools and from a general point of view thought that C was a particularly excellent wool. All three wools were expensive, the highest price (on a clean wool basis) being that of C. For the manufacture of face cloths, however, A and B were decidedly superior, and he associated a well-defined crimp with good milling properties.

Buyer 3. C was ideal for his purposes (top manufacture). A and B were outside the range of types he normally employed; they were thought to be finer than C, but even if they had the same dimensions, he would still prefer C.

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Aeration Recovery of Lanolin from Wool Scour Liquors

C. A. Anderson

Commonwealth Scientific and Industrial Research Organization, Division of Textile Industry, Wool Research Laboratories, Geelong, Australia

Abstract

Further investigation of the aeration process has resulted in an improved design for a continuous recovery plant. On a pilot scale the improved design has permitted throughput rates about 2½ times greater than previous designs, with equal recovery efficiencies.

Introduction

Previous work [2] has shown that lanolin recoveries of 45–60% can be obtained by aeration of wool scour liquors in modified mineral flotation cells. Batch tests using a Denver laboratory flotation machine showed that in the range 20°–30° C., the percentage of lanolin recoverable from a liquor was independent of temperature, pH, dirt concentration, soap concentration, and the presence of added salts. Continuous recovery tests in a battery of 4 cells showed that maximum recovery was obtained with cell residence times between 4 and 10 min. Cell residence time was calculated by dividing the effective cell volume by the liquor throughput rate.

On the basis of these experiments, three industrial plants were built, from which it was shown that cell residence times much longer than those found in laboratory experiments were necessary for maximum recovery [1].

The cell residence time had to be increased even more when the liquors had high soap contents or had decomposed through aging. Consequently, the throughput rates of liquor in the industrial units were lower than expected.

This paper describes work undertaken to improve the throughput capacity of the aeration cells. Preliminary work was done using a single laboratory cell for batch tests, and from the results obtained a pilot plant of improved design was constructed. The performance of this plant using a wide variety of commercial liquors is described.

Laboratory Methods for Estimating Recovery

The following laboratory technique was used for estimating lanolin recovery: 750 ml. of scour liquor at 30° C. was aerated for 15 min. in a 500-g. Denver Laboratory Flotation Machine. The aerated liquor was then transferred to a separating funnel, vacuum applied to the space above the liquor, and the contents allowed to settle for 1 min. The application of vacuum enabled the froth to separate from the bottom liquor more quickly than with gravity alone. The bottom liquor was returned to the cell, reaerated for a further 15 min., and the froth again settled and removed as above. Recovery was calculated by difference between the lanolin content of the starting liquor and that of the final bottom liquor. Using this technique, longer or more numerous aerations did not materially increase the recovery. It is believed that the figure obtained by this method represents the maximum amount of lanolin recoverable by aeration.

When the effects of time of aeration and removal of froth were studied, the liquor was allowed to drain by gravity without vacuum for 1 min. before removal of froth.

Effect of Additions to Liquor on Maximum Recovery

Evans and Ewers [2] unsuccessfully attempted to increase recovery of lanolin by adding various substances to the liquor before aeration. As the recoveries obtained are often as low as 50%, further work on this aspect was carried out using substances likely to affect emulsion stability or foam properties of scour liquors.

Foam Stabilizers

The addition of 0.1–0.4% (wt./vol.) of egg albumen, gelatin, and gum tragacanth to commercial

scour liquors had no effect on the maximum recovery, while sodium carboxymethyl cellulose reduced the recovery.

Foam Breakers

Pine oil, iso-octanol, n-butanol, eucalyptus oil, Irgafoamal T (Geigy Co. Ltd.), and silicone antifoam M430 (I.C.I.A.N.Z.) in concentrations of 0.1–1.0% (vol./vol.) were each added to scour liquors before aeration. Recoveries obtained at the optimum concentrations are given in Table I.

Although pine oil, n-butanol, and silicone M430 increase recovery, the high concentrations required would make their commercial use impracticable.

Cationic Surface Active Agents

Additions of 0.1–0.3% (wt./vol.) of Sapamine WL (Ciba), Eulan NK (Farbenfabriken Bayer Leverkusen), cetyl dimethyl benzyl ammonium bromide, and lauryl pyridinium chloride had no effect on recovery.

Suint

Merino 64's fleece wools of varying suint contents were scoured in the laboratory and the liquors aerated for two 15-min. periods. Recovery was not affected by variations in the suint content of the raw wool which ranged from 0 to 8.0%.

From these results and those of Evans and Ewers it appears that a significant increase in lanolin recovery cannot be obtained by making additions to the scour liquors before aeration.

TABLE I. Effect of Foam Breakers on Recovery

Addition	Optimum conc'n, %	Recovery, %
Irgafoamal T	0.2	58
Eucalyptus Oil	0.5	57
Pine Oil	0.5	64
Butanol	0.5	60
Silicone M430	0.1	62
Control	—	57

TABLE II. Effect of Impeller Speed on Recovery

Wax content of liquor, 1.97%; wool, scoured Merino 64's fleece.

Aeration time	Recovery (%) at various impeller speeds (r.p.m.)		
	700	1700	2600
2 × 2 min.	13	38	42
2 × 5 min.	42	58	56
2 × 10 min.	48	65	67
2 × 15 min.	64	73	73

TABLE III. Effect of Impeller Design on Recovery

Impeller	Aeration time	Recovery, %
Denver	2 × 15 min.	50
Fagergren	2 × 15 min.	34
	2 × 30 min.	42
	3 × 30 min.	43
Centrifugal		
clockwise	2 × 15 min.	47
anticlockwise	2 × 15 min.	50

Effect of Plant Design on Recovery

Provided recoveries greater than 45% are maintained, the economic success of the aeration process depends on the liquor throughput capacity of the cells. The effects of certain aspects of cell design on throughput capacity were therefore investigated.

Impeller Speed

In all previous tests, liquors were aerated for two 15-min. periods at an impeller speed of 1700 r.p.m. To ascertain the effect of impeller speed on recovery, liquors were aerated for various times at different speeds. After each aeration period, the froth was removed after gravity settling for 1 min.

The results given in Table II show that there is no improvement in recovery by increasing the impeller speed from 1700 r.p.m. to 2600 r.p.m. However, reducing the impeller speed to 700 r.p.m. gave lower recoveries, especially with shorter aeration times.

TABLE IV. Effect of Cell Residence Time on Recovery

Liquor	Liquor feed rate, gal./hr.	Residence time in each cell, min.	Recovery, %
Liquor A	112	35	59
	116	34	58
	150	26	50
	225	17	35
Liquor B	90	43	48
	110	35	47
	180	21.5	30

Liquor A: Wool scoured, Merino locks/crutchings; soap content (Na + Ca) 0.2%; wax content 2.63%

Liquor B: Wool scoured, Crossbred lambs; soap content (Na + Ca) 0.3%; wax content 1.72%

TABLE V. Effect of Residence Time in Laboratory Cell on Recovery

Wax content of liquor, 1.97%; wool, scoured Merino 64's fleece.

Cell residence time for each aeration, min.	No. of aerations	Recovery, %
2½	2	47
5	2	58
10	2	65
15	2	73
30	2	73

Impeller Design

Aliquots of liquor were aerated in either the Denver laboratory cell, a Fagergren laboratory test machine, or a cell with a centrifugal impeller as described by Evans and Ewers. Tests were done with both clockwise and anticlockwise rotation of the latter impeller.

It was noticed that the aeration capacity of the Fagergren impeller was the lowest of the three and that the centrifugal impeller rotating anticlockwise caused greater turbulence than the others. The results of Table III show that the Denver and the centrifugal impeller are equally effective and better than the Fagergren.

Cell Residence Time and Removal of Froth

As liquor throughput is inversely proportional to cell residence time in any cell, the effect of this factor on recovery was investigated in an industrial plant and by laboratory tests.

In the first case, liquor from the first bowl of a commercial scour was cooled rapidly to 30° C. and pumped to storage. The liquor was then aerated in a modified four-cell Denver No. 18 flotation machine. Two cells were used as recovery cells and two as washing cells. Recoveries obtained from two liquors are given in Table IV.

The results show that very low recoveries are obtained even when the cell residence time is 17 min. with Liquor A and 21.5 min. with Liquor B.

In the laboratory tests, samples of liquor from an industrial scour were aerated for various times in the Denver laboratory cell. The results obtained are given in Table V.

It is seen that maximum recovery is obtained in laboratory scale tests by aerating for two 15-min. periods.

TABLE VI. Effect of Settling Time on Recovery

Settling time, min.	Recovery, %
0	6.3
1	30
2	36
4	41
10	40
90	43

TABLE VII. Effect of Settling Before Froth Removal on Recovery

Aeration time	Settling time, min.	Recovery, %
2 × 2½ min.	0	40
2 × 2½ min.	1	47
4 × 2½ min.	0	49
4 × 2½ min.	1	71
2 × 5 min.	0	49
2 × 5 min.	1	58
3 × 5 min.	0	60
3 × 5 min.	1	69

Although the laboratory tests indicated that two aeration periods each of 15 min. removed all the recoverable lanolin from a scour liquor, results obtained in the industrial tests showed that much longer aeration periods were necessary. In the laboratory tests, froth was removed after vacuum flotation, whereas in the industrial plant, froth was separated after gravity settling. The effect of this difference in method of froth removal on the rate of recovery was therefore investigated by aerating liquors two, three, or four times for various periods, froth being removed after the aerated liquor had stood for 1 min. without vacuum flotation. Recoveries obtained from these multiple aerations are plotted against the aeration periods in Figure 1.

It is seen that all recoverable lanolin—73%—is removed by four 3-min. aerations, three 10-min., or two 20-min. aerations.

As the liquor throughput capacity of a bank of cells in series is determined by the residence time of liquor in each cell, it is clear that of the systems tested, the four-cell unit with froth removal after each aeration has the greatest production. In fact, four cells in series have at least six times the capacity of two cells. Obviously the total aeration time is not the only factor in determining recovery rate; removal of froth between aeration treatments is also important.

The influence of settling time on recovery was

then determined by aerating liquors for 10 min., rapidly transferring them to a separating funnel, and withdrawing bottom liquor samples after various times. Results are given in Table VI. Table VII shows the effect of varying both the time of aeration and the settling time.

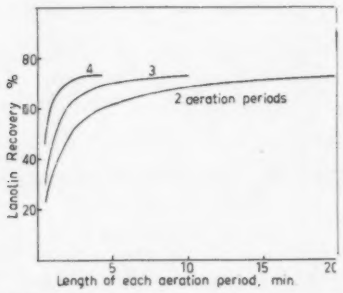

Fig. 1. Recovery of lanolin in laboratory aeration tests plotted against the length of each aeration period. Recoveries were determined after two, three, or four aeration periods.

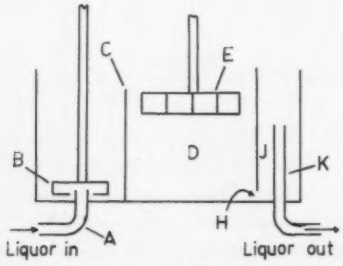

Fig. 2. The basic cell unit of the pilot aeration plant.

It is seen that maximum recovery can be obtained even with short cell residence times provided there is a short settling time before the partially dewaxed liquor is separated from the froth. It is also seen that, under the relatively static conditions of the laboratory tests, a settling period between 1 and 4 min. is satisfactory; however, it seemed likely that, in a continuous plant, longer settling periods would be necessary because of turbulence set up by the continuous flow of liquor.

Continuous Recovery Tests in Pilot Plant

Based on the above results, a pilot plant was constructed in which feed and recirculation could be readily modified. The basic cell unit is shown in Figure 2. The experimental aeration plant shown in Figures 3 and 4 consists of six such units.

When scour liquor at 30° C. is sucked, together with air, through pipe A (Figures 2 and 3) by the action of the centrifugal impeller B, a froth is formed which passes over weir C into a settling compartment D, where a slowly revolving open-bladed impeller E (27 r.p.m.) accelerates the breakdown of the froth. The partially dewaxed liquor drains from

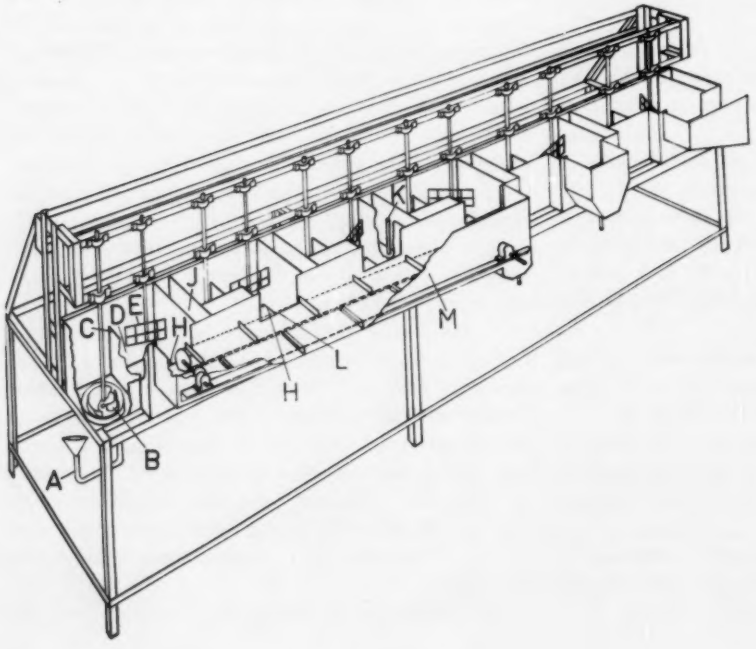

Fig. 3. Sectional diagram of the pilot aeration plant for the recovery of lanolin from wool scour liquors.

the froth, passes through an opening H into the compartment J, and then down the liquor overflow pipe K which is connected to another impeller. The lanolin-rich froth in D builds up and flows over the lip L into the launder M which leads to a washing cell. To assist in transportation of the froth down the launder M, a moving endless chain with scraper blades is used. The degreased liquor overflowing from each cell is reaerated in the following cell. At a liquor feed rate of 13 gallons/hr. to this plant, each aeration period was approximately 4 min. and froth settling time in compartment D was approximately 7 min.

Many systems of liquor feed and recirculation were tested, the best being illustrated in the flow diagram shown in Figure 5. In this system, froth from the first four cells is washed by counter current water in the last two cells.

Plant capacity and quality of product depend on three factors: liquor feed rate, wash water feed rate, and froth settling in compartment D, which is controlled by the height of pipe K (Figure 3). When the froth in D is low in lanolin content, the pipe K is lowered. For maximum throughput, the overflow pipe in the first cell should be as low as possible, the height being progressively raised in the following cells. In the last cell the overflow is within half an inch of the froth level in the settling compartment D.

This plant differs from the original [2] and the existing industrial models [1] in two respects: a settling compartment is provided in each cell, so that the froth and the liquor are almost completely separated before the liquor is reaerated, and the froth is not recirculated through the recovery cells but passes immediately to the washing cells.

The performance of this plant was evaluated on various samples of liquor from commercial scourers handling a wide variety of wool types.

The liquor was pumped to a storage tank and cooled to 30° C. by a heat exchanger. The feed rate to the first cell was increased until the optimum amount of froth was delivered to the froth launder. If the washing cells were working below capacity the level of froth in the launder fell continuously; on the other hand, excessive liquor feed rates caused a bank up of froth in the launder. Laboratory aeration tests on the effluent from the third recovery cell at optimum feed rate showed that all recoverable lanolin had been removed. In effect, therefore, three recovery and two washing cells were used.

Froth from the last cell was collected in a 44-gallon tank and dispersed by heating to 90° C. in an equal volume of 2% sodium carbonate solution. From lanolin contents and volumes of dispersion and initial liquor, the percentage recovery was calculated. Details of recovery from several liquors are given in Table VIII.

The outstanding feature of these results is the high capacity of the pilot plant. With cells of the same volume and with the same impellers as used by Evans and Ewers, it has a throughput in the range 13–26 gallons/hr. compared with 4–10 gallons/hr. in the Evans' and Ewers' pilot plant.

Data from Scour 2 (Table VIII), plotted in Fig-

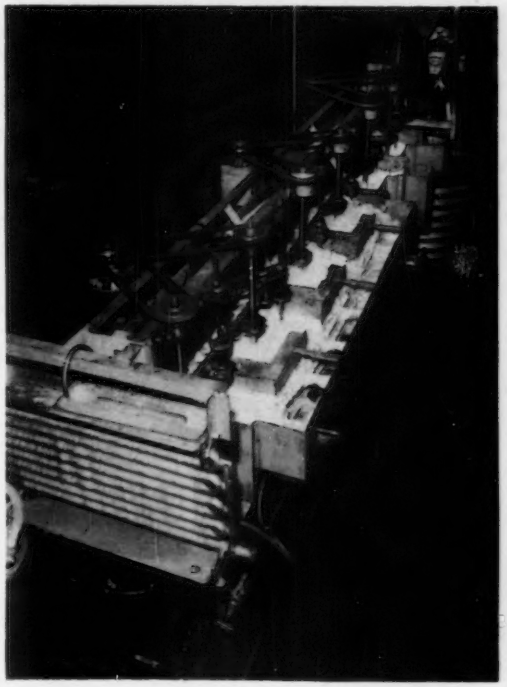

Fig. 4. Pilot aeration plant for the recovery of lanolin from wool scour liquors.

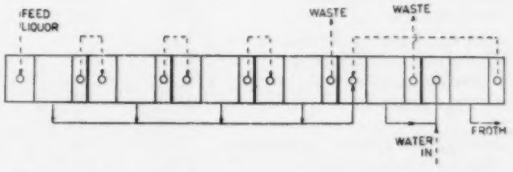

Fig. 5. Flow chart of scour liquor and froth in pilot aeration plant. Flow path of aerated liquor is shown by dotted line; flow path of froth is shown by continuous line.

ure 6, also show that, for constant wool type characteristics—suint, dirt, and wax—and scouring conditions, the lanolin production is dependent on the wax content of the liquor. The results also confirm earlier conclusions [1] that recovery is dependent on soap content and degree of agitation of the liquor.

Initial laboratory experiments showed that the degreased effluent from Cell 3 had detergent properties which opens the possibility of continuous recirculation of liquor through the aeration plant and back to the scouring bowl. A flow sheet for such a system is shown in Figure 7.

Summary

An improved pilot plant for the recovery of lanolin from wool scour liquors has been constructed as a result of further investigation of the aeration process. It differs from that of Evans and Ewers and the industrial units based on their work in two respects: a settling compartment is provided in each cell, so that the froth and the liquor are almost completely separated before the liquor is reaerated, and the froth is not recirculated through the recovery cells but passes immediately to the washing cells.

Attempts to improve lanolin recovery by additions of foam stabilizers, foam breakers, cationic surface active agents, and suint were unsuccessful.

The amount and rate of lanolin recovery are affected by impeller design, impeller speed, aeration time, and froth settling and removal between multiple aeration treatments.

In a Denver laboratory flotation cell used batchwise, maximum recovery was obtained by aeration

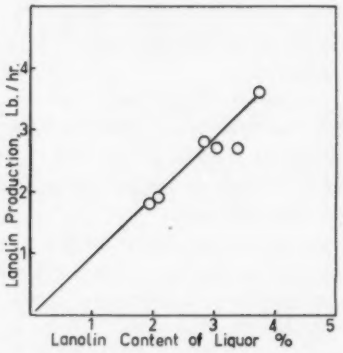

Fig. 6. Production of lanolin from the pilot plant plotted against the lanolin concentration of the initial liquor.

TABLE VIII. Pilot Plant Recovery from Commercial Scour Liquors

Scour	Wool type	Wax content, %	Feed rate, gal./hr.	Recovery, %	Lanolin production, lb./hr.	Comments
1.	Merino stains	1.73	13	33	0.75	All carbonizing types
	Merino stains	2.04	14	50	1.4	
	Comeback stains	2.67	13.5	34	1.2	Agitation during scouring vigorous.
	Comeback crutchings	1.38	23	33	0.9	Soap content high, approx. 0.3%
	Merino crutchings	2.49	15.5	44	1.6	
	Merino lambs	2.86	16.5	51	1.9	
2.	Merino fleece 64's	2.07	13	66	1.8	Combing fleece wools
	Merino fleece 58's	2.20	13.3	65	1.9	
	Merino fleece 58's	2.84	15.5	65	2.8	Little agitation, soap content ap-
	Merino fleece 64's	3.04	15	60	2.7	prox. 0.15%
	Merino fleece 64's	3.40	13.5	59	2.7	
	Merino fleece 64's	3.76	12.5	76	3.6	
	Merino fleece 64's	>4	11.5	—	3.9	
3.	Merino locks/crutchings	1.54	20	48	1.5	Woolen types
	Merino/comeback locks	1.27	26	50	1.6	
	Merino locks	1.40	26	54	1.9	
	Merino locks/comeback lambs	1.44	18	59	1.6	Little agitation
	Comeback crutchings	1.20	15	58	1.1	
	Comeback lambs	1.23	20	62	1.5	
	Comeback lambs	1.53	14	61	1.3	
4.	Merino lambs/locks/crutchings	2.20	16	50	1.8	All carbonizing types
	Merino locks/crutchings	2.90	13.3	57	2.2	
	Merino lambs/locks/crutchings	3.09	14.8	51	2.1	Agitation gentler than Scour 1 but
	Merino lambs/locks/crutchings	3.90	13.3	51	2.7	more vigorous than Scour 3
	Merino lambs	2.36	16	40	1.5	

at an impeller speed of 1700 r.p.m., for four 3-min. periods, provided the aerated liquor was allowed to stand for 1 min. and the froth removed before each reaeration. If only two aeration treatments were given, each had to be of 20 min. duration to obtain the maximum recovery.

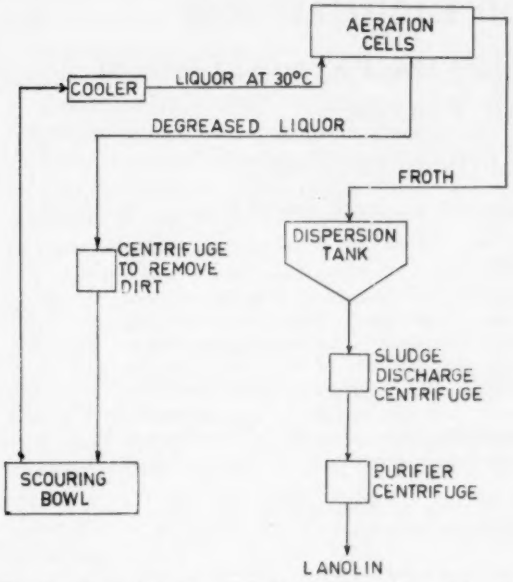

Fig. 7. Flow sheet for a continuous scouring and lanolin recovery process.

In the improved pilot plant maximum recovery from commercial liquors was obtained at feed rates between 13 and 26 gallons/hr. depending on the type of liquor. A Merino 64's fleece wool liquor containing 2.84% lanolin gave 65% recovery at a liquor feed rate of 15.5 gallons/hr. The original plant of the same physical size had a throughput capacity of only 4–10 gallons/hr.

Acknowledgments

The author wishes to thank Dr. M. Lipson, Chief, C.S.I.R.O., Division of Textile Industry, Geelong and Dr. G. F. Wood for many helpful discussions. The assistance of Mr. D. J. Smith with the experimental work is gratefully acknowledged.

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The Physical State of Direct Dyes in Viscose and its Influence on Lightfastness

Part I: A Method of Examining the Physical State of Direct Dyes in Viscose

Leonard Weissbein and Glenn E. Coven

Bound Brook Research Laboratories, American Cyanamid Company, Bound Brook, New Jersey

Abstract

As part of a study on the factors determining the lightfastness of dyes on cellulosic materials, a means of examining the physical state of direct dyes in viscose was developed which makes use of dyed ultrathin films as primary specimens in the electron microscope.

When this method was used to examine the physical state of two direct dyes in viscose, their physical state was found to differ markedly. Aggregates of one dye could not be detected in the viscose films at a resolution limit of about 30 Å, whereas aggregates of the other dye were plainly visible in viscose films dyed under the same conditions. The apparently unaggregated dye exhibited considerably poorer lightfastness on rayon than the one which aggregated in viscose.

The results suggest the use of this method of study to investigate the influence of the physical state of direct dyes in viscose on their lightfastness.

Introduction

Many independent studies have been made on the chemistry of the light fading of dyed cellulosic materials [1, 5, 7–10, 14, 16, 17, 20, 27]. It has been generally concluded that the dyes on these materials are converted to their fading products upon exposure to sunlight primarily by a complex photo-oxidative mechanism in which oxygen and water are involved.

There is experimental evidence that the good lightfastness obtained with vat and naphthol dyeings, in which the dyes are insolubilized and "developed" upon application to form large crystalline aggregates within the fibers, is a result of the aggregated state of the dyes in the fibers [4, 11, 12, 15, 19, 21, 22, 24, 26]. The photochemical decomposition of such dyes must occur at the surface of the dye aggregates. Thus, the more the dye is aggregated in the material, the better its lightfastness, because the surface area per unit mass of dye decreases as its aggregate size increases.

From their studies of the kinetics of fading, Baxter and Giles et al. [2, 3, 13] deduced that water-soluble dyes, such as the direct dyes, exist at least in part as aggregates or crystals of submicroscopic size within the dyed fibers. They also concluded that lightfastness, even of materials dyed with water-soluble dyes, is more dependent upon the physical state (particle size distribution) of the dyes within the fibers than on the inherent resistance of the dye molecules to photochemical decomposition.

Opposing this view, present dyeing theory favors a mechanism in which direct dyes are monomolecularly sorbed on the cellulose chains of the fibers during dyeing [6, 25]. Valko [23] has cited some evidence, although not conclusive, that the dyes remain in this state within the fibers even after dyeing.

Clearly, more direct evidence that water-soluble dyes aggregate in cellulose is required if it is to be established that the physical state of the dyes in cellulosic materials is the factor mainly responsible for their lightfastness. The object of this study was to determine whether aggregation of direct dyes could be detected in cellulose with the electron microscope.

Experimental Method

Since methods of ultrathin sectioning dyed fibers had not yet been developed sufficiently for use in high resolution electron microscopy, ultrathin films were prepared from viscose dope taken from a commercial batch about to be spun into rayon. A special technique and apparatus made it possible to dye the

viscose films with direct dyes under conditions corresponding to those frequently used in commercial practice. The dyed films were then used as primary specimens in the electron microscope.

The cellulose of which the viscose films are composed is structurally similar to that of rayon fibers in almost every respect. In fact, the films differ from rayon only in that their polycrystalline polymer structure is unordered, whereas that of rayon fibers is partially ordered as a result of spinning and drawing. It can be reasonably assumed from this similarity that aggregation of a dye as observed in the viscose films would also occur in rayon dyed under the same conditions.

Ultrathin Film Preparation

Ultrathin viscose films suitable for this study were prepared as follows.

A small drop of viscose dope was placed upon a microscope slide. It was smeared to a thin film with the convex surface of a positive spherical lens of about one diopter. The smearing was accomplished by moving the lens back and forth over the glass slide. One edge of the film was left thick, while the rest was spread out as thinly as possible. The slide was then immersed in a warm coagulating bath containing 10% H_2SO_4, 5% $ZnSO_4 \cdot 7H_2O$, and 20% Na_2SO_4.

Upon coagulation, the thinnest portion of a properly prepared film would adhere to the glass slide, while the rest of it would peel off the slide and float freely in the bath. Peeling of the film usually started at its thick edge. The slide with film attached was put through three successive rinses by immersion in distilled and demineralized water.

In the final rinse bath, 10–20 stainless steel specimen grids of $\frac{1}{8}$-in. diameter were placed on the slide under the floating film. The slide was then raised out of the rinsing bath, attached part first, so that the film spread evenly over the grids and trapped them on the slide. The slide and film assembly was set aside to drain and dry. When the specimen grids were then lifted carefully from the slide, they remained almost completely covered by an adhering film of dried viscose. Viscose films prepared in this manner were estimated to be about 500–1,000 Å thick.

Dyeing the Ultrathin Films

The following method was developed for dyeing the ultrathin viscose films with direct dyes under conditions corresponding to those frequently used in commercial practice.

Four film specimens, supported on specimen grids, were mounted in the special holder shown in Figure 1. This stainless steel holder was designed to clamp the films to the grids at their periphery to minimize

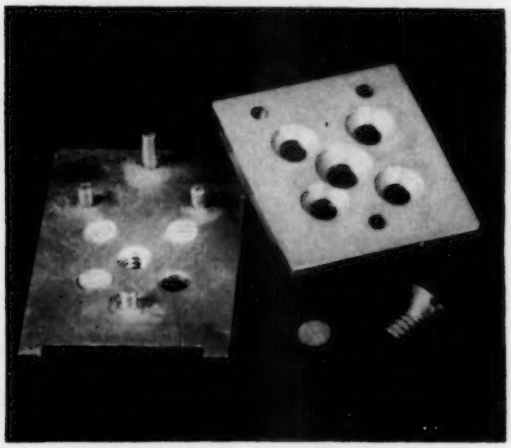

Fig. 1. Holder with specimen grids.

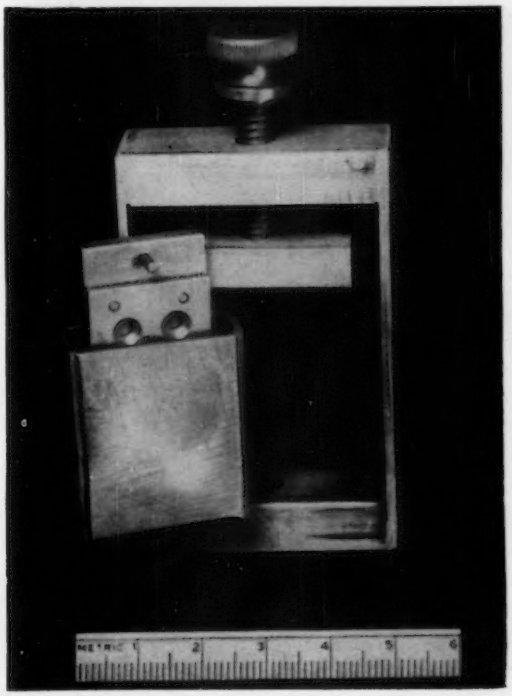

Fig. 2. Dye cell with holder and clamp for sealing.

loss or damage of the films during dyeing. The holder was then placed in a 4-cc. stainless steel dye cell shown in Figure 2, which was sealed at the top with a clamp to prevent liquid loss during dyeing.

In commercial practice, the weight of the material to be dyed is used as the basis for establishing dyebath conditions, which include dye and salt concentrations and dyebath volume. Since the ultrathin films had virtually no measurable weight of their own, a 0.20-g. piece of purified rayon fabric was placed in the dye cell along with the films to establish the fabric weight basis for the dyebath conditions.

A 4-cc. sample of a freshly prepared dye solution was pipetted into the cell. The solution sample contained 1.5% dye, which had been purified by the technique of Robinson and Mills [18], and 20% sodium chloride on the weight of rayon fabric in the cell. The dyebath conditions were selected to represent those frequently used in a commercial beck dyeing operation.

The dye cell was sealed and placed on an oscillating platform in a controlled temperature bath at 120° F. The temperature was raised to 180° F. in 10 min. and held there for 1 hr. After being dyed, the film specimens were given four successive rinses in cold distilled water and air dried before they were removed from the specimen holder for examination in the electron microscope.

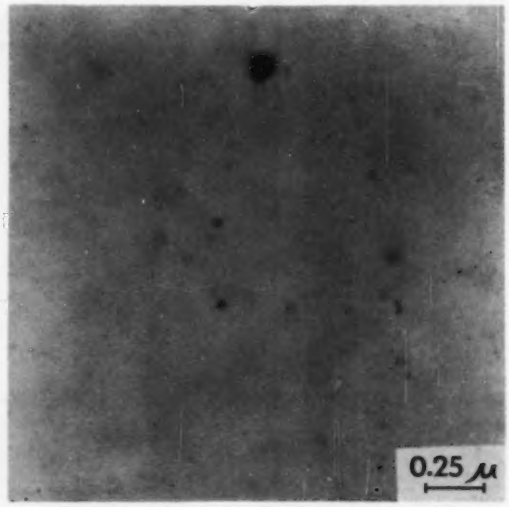

Fig. 3. Ultrathin viscose film "dye control."

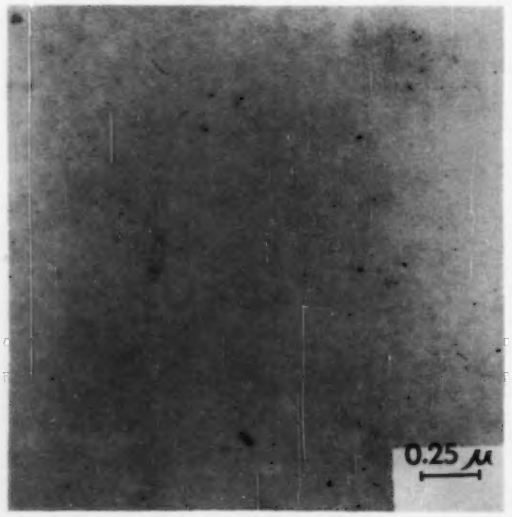

Fig. 4. Ultrathin viscose film dyed with Direct Sky Blue FF.

Results and Conclusions

Figures 4 and 5 are electron micrographs of ultrathin viscose films dyed with Direct Sky Blue FF (Color Index 24410) and Direct Blue 4GL (Color Index 34200) by the method described. Figure 3 is an electron micrograph of an ultrathin viscose film exposed to similar conditions, but in a bath that contained no dye. A film treated in the latter manner will be referred to as a "dye control."

The electron micrographs shown in Figures 3–6

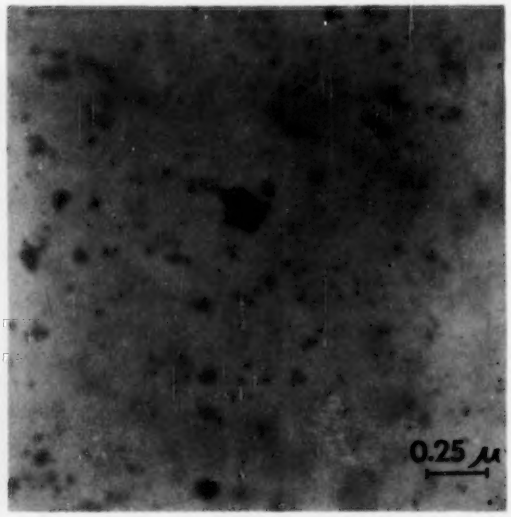

Fig. 5. Ultrathin viscose film dyed with Direct Blue 4GL.

were taken with an RCA Model EMU-2D electron microscope at an initial magnification of 20,000 ×, with a resolution limit of about 30 Å.

The electron micrograph of the viscose film dyed with Direct Sky Blue FF (Figure 4) is virtually indistinguishable from that of the dye control (Figure 3). Except for a few occasional specks of foreign material, both fields appear blank and structureless. Aggregates of this dye, if they do form in viscose, are either of a maximum size below the limit of resolution or of such low electron scattering power as to be indistinguishable from the viscose film.

The micrograph shown in Figure 5 constitutes direct evidence of aggregation of a water-soluble dye in viscose dyed under conditions used in commercial practice. A comparison of Figure 4 with Figure 5 illustrates how markedly direct dyes can differ in their tendency to aggregate in viscose when applied under these conditions.

Close examination of the aggregates of Direct Blue 4GL shown in Figure 5 reveals that they are actually dense clusters of minute dye particles or dye crystals of a size close to the limit of resolution. Although the dye aggregates are rather large, there is evidence that they were formed within the viscose film. Their general appearance is one of aggregates embedded in or covered by a second phase. Aggregates sitting on the surface of the film should be more clearly defined than is indicated in Figure 5.

Figure 6 is an electron micrograph of the same field shown in Figure 5 taken after the viscose film had been lightly shadowed with uranium (at an angle of 20°) to reveal its surface structure. Close comparison of Figure 5 with Figure 6 gives further evidence that the aggregates of Direct Blue 4GL were formed within the polymer structure of the viscose film. An aggregate merely deposited on the surface of the film would cast a sharp shadow. Few of the dye aggregates cast sharp shadows, suggesting that most of the aggregates are either inside the film or are too thin to cast sharp shadows. The superimposition of the surface polymer structure of the film, made visible in Figure 6, on these aggregates indicates that they are inside the film and accounts for their lack of definition in Figure 5.

Some of the dye aggregates appear to be just beneath the surface of the film. Their presence there results in a raising of the polymer structure covering them to form mounds or nodes on the film surface. The occurrence of these nodes on the film surface

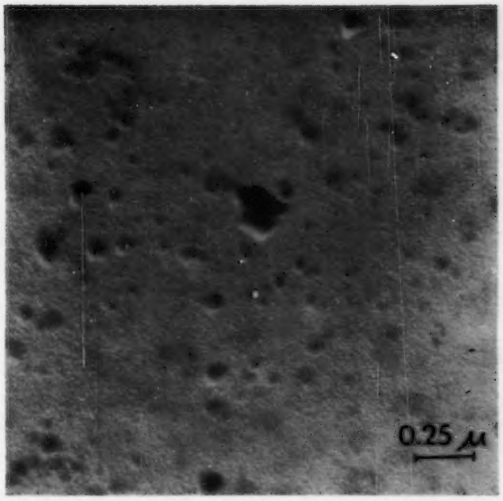

Fig. 6. Ultrathin viscose film dyed with Direct Blue 4GL and shadowed with uranium.

suggests that the dye aggregates were formed when the polymer chain network of the film was in the water-swollen state. The viscose polymer chain network is apparently capable of considerable distention when swollen by water. The nodes are probably a result of contraction of the polymer network around the aggregates upon drying.

Direct Sky Blue FF and Direct Blue 4GL were applied to spun rayon fabric under the same conditions selected for dyeing the ultrathin viscose films. The Sky Blue FF dyeings were noticeably faded after 10 hr. of exposure in a Fade-Ometer, whereas the dyeings of Blue 4GL showed no noticeable fading until 60 hr. of exposure. This difference in lightfastness could have resulted from a difference in either the physical state of the dyes in the fibers or the chemical nature of the dyes. It might be possible to determine which factor is more important by extending this method of study to a number of direct dyes of widely diverse chemical composition.

Acknowledgments

The viscose dope used to produce ultrathin films for this study was generously supplied by Mr. Frederick Morehead, of American Viscose Corporation. The procedure for making the films was suggested by one used by Mr. Morehead and Dr. Charles Maresh of American Cyanamid Company some years ago. This manuscript has profited by the careful review and criticisms of Dr. S. J. O'Brien. The valuable

assistance of Mrs. Marian Anderson in the preparation of dyed ultrathin films is gratefully acknowledged.

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Part II: The Relation Between the Physical State of Direct Dyes in Viscose and Lightfastness

Abstract

The methods of Part I, which combined electron microscopical examination of dyed ultrathin viscose films with lightfastness measurements on corresponding rayon dyeings, were extended to several direct dyes of diverse chemical structure.

Only two of the nine dyes studied did not appear to aggregate, i.e., did not form aggregates detectable in the dyed viscose films at a resolution limit of about 30 Å. The apparently unaggregated dyes exhibited considerably poorer lightfastness on rayon than the others which aggregated in viscose.

The results support the idea that the physical state of direct dyes in viscose is an important factor in determining their lightfastness on this material.

Introduction

Giles and coworkers [1, 2, 3] have postulated that water-soluble dyes, such as the direct dyes, exist at least in part as aggregates or crystals of submicroscopic size within dyed fibers. They further postulated that the variation in lightfastness among water-soluble dyes on a given substrate arises more from differences in their physical (aggregation) state in the substrate than from differences in their chemical nature.

In the previous paper [6], it was shown that aggregates of a water-soluble (direct) dye could be detected in dyed ultrathin viscose films with the electron microscope. Reasons were given for assuming

that aggregation of the dye would also occur in rayon dyed under the same conditions. The present paper combines electron microscopical examination of dyed ultrathin viscose films with lightfastness measurements on corresponding rayon dyeings. Its purpose is to investigate the relation between the physical state of direct dyes in viscose and their lightfastness on this material.

Experimental Method

Several direct dyes of diverse chemical structure were selected and applied to spun rayon fabric under conditions chosen to represent those of a commercial beck dyeing operation. The dyes selected and their chemical structures are given in the first two columns of Table I. The dyes were obtained as commercial types and purified by the technique of Robinson and Mills [5].

The rayon dyeings were made by the following standard procedure.

Pieces of scoured and bleached spun rayon fabric weighing 3.00 g. were wet out in distilled water. The wet-out rayon pieces were immersed in 60-cc. dyebaths containing 1.5% dye and 20% sodium chloride, both based on the weight of the rayon. The temperature of the baths, 120° F. when the rayon pieces were immersed, was raised to 180° F. in 10 min. and maintained there for 1 hr. The dyed pieces were then removed, rinsed several times in distilled water, and air-dried.

The rayon dyeings were all exposed simultaneously in a Fade-Ometer. In each case, the exposure time which produced a break, i.e., a perceptible

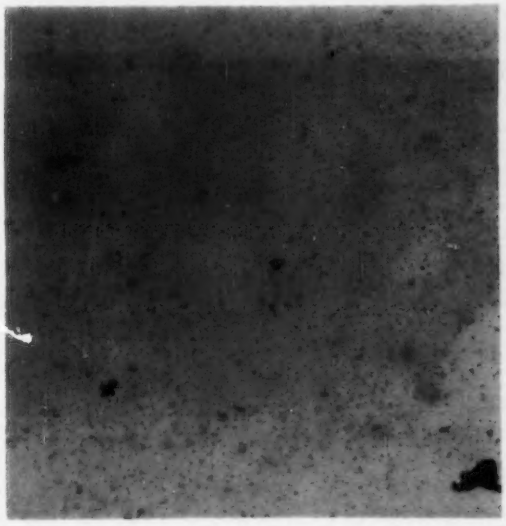

Fig. 1. Ultrathin viscose film dyed with Direct Violet N.

TABLE I. Summary of Results

Dye	Structure	Light-fastness on rayon*	State of aggregation in viscose†
Direct Violet N (C.I. 22570)	Benzidine ⇌ (acid) 6-amino-4-naphthol-2-sulfonic acid (2 moles)	40	Aggregated
Direct Violet RM	Anthranilic acid → 6,6′-iminobis-(1-naphthol-3-sulfonic acid) copperized	60	Aggregated
Direct Brown R	7-Aminonaphthalene-1,3-disulfonic acid → aniline → cresidine, phosgenated	80	Aggregated
Direct Blue RM	*o*-Dianisidine ⇌ 8-acetamido-1-naphthol-3,6-disulfonic acid (2 moles), copperized	80	Aggregated
Direct Blue R	*o*-Dianisidine ⇌ 8-acetamido-1-naphthol-3,6-disulfonic acid (2 moles)	10	Apparently unaggregated
Direct Yellow RL (C.I. 29025)	3-Amino-1,5-naphthalene disulfonic acid → *m*-toluidine, phosgenated	60	Aggregated
Direct Sky Blue FFM	*o*-Dianisidine ⇌ 8-amino-1-naphthol-5,7-disulfonic acid (2 moles), copperized	60	Aggregated
Direct Sky Blue FF (C.I. 24410)	*o*-Dianisidine ⇌ 8-amino-1-naphthol-5,7-disulfonic acid (2 moles)	10	Apparently unaggregated
Direct Blue 4GL (C.I. 34200)	2-Amino-*p*-benzenedisulfonic acid → 8-amino-2-naphthalenesulfonic acid → 1-naphthylamine → (alk) 7-anilino-4-naphthol-2-sulfonic acid	60	Aggregated

* As measured in terms of Fade-Ometer hours of exposure to the break.
† As observed by electron microscopical examination of dyed ultrathin viscose films.

change in shade, was taken as the measure of the lightfastness of the dyeing.

Ultrathin viscose films were prepared and dyed with the dyes listed in Table I under conditions corresponding to those used to make the rayon dyeings. The methods for preparing and dyeing the viscose films have already been described in detail in the previous paper [6].

The dyed viscose films were examined in the electron microscope for dye aggregation, and the results were compared with the light fading results obtained with the rayon dyeings.

Results and Conclusions

The third column of Table I gives the lightfastness, in terms of Fade-Ometer exposure hours to the break, of the rayon dyeings made with the dyes listed in the first column. Figures 1 through 7 are electron micrographs of ultrathin viscose films dyed with the first seven of the dyes listed in Table I. Electron micrographs of viscose films dyed with the other two dyes, Direct Sky Blue FF and Direct Blue 4GL, were shown previously ([6], Figures 4 and 5). All electron micrographs were taken at an initial magnification of 20,000× with a resolution limit of about 30 Å. The results are summarized in the last column of Table I, which indicates whether or not each dye aggregated in the dyed viscose film.

Of the nine dyes examined, seven were aggregated in the viscose films. Examination of the same fields shown in Figures 3 and 6 after lightly shadowing the viscose films with uranium to reveal their surface structure gave results similar to those obtained with Direct Blue 4GL ([6], Figures 5 and 6). Those results indicated that the dye aggregates had formed within the polymer structure of the film and were not merely surface deposits. The long needle-like structures prominent in Figure 2 are crystals of Direct Violet RM. These dye crystals, which were revealed by uranium shadowing to be present on the surface of the dyed viscose film, are easily distin-

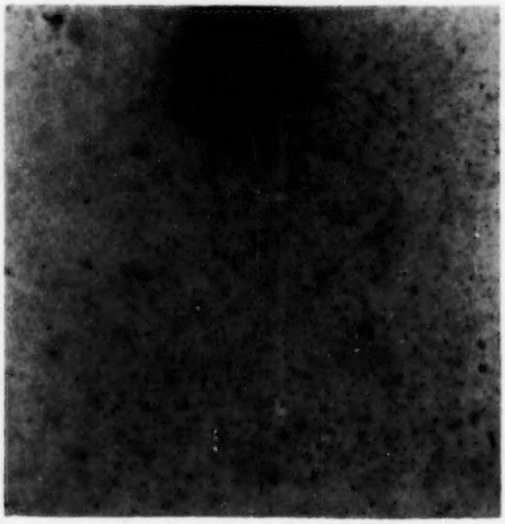

Fig. 3. Ultrathin viscose film dyed with Direct Brown R.

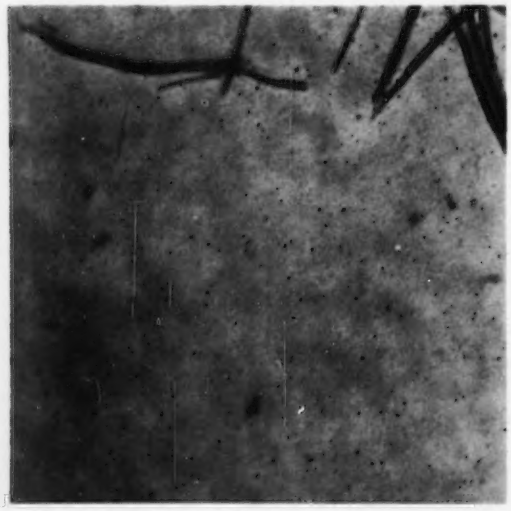

Fig. 2. Ultrathin viscose film dyed with Direct Violet RM.

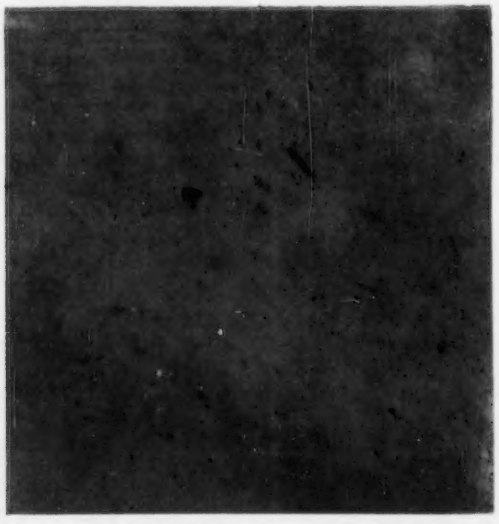

Fig. 4. Ultrathin viscose film dyed with Direct Blue RM.

guishable from the smaller dye aggregates that were formed within the polymer structure of the film.

The large dye aggregates appearing in some of the viscose films (see Figures 1, 3, and 6) are probably clumps of dye particles or dye crystals of a much smaller ultimate size. The size of these ultimate dye particles cannot be determined from the electron micrographs. It is also impossible to determine the proportion of dye in the viscose films that had aggregated sufficiently to be detectable.

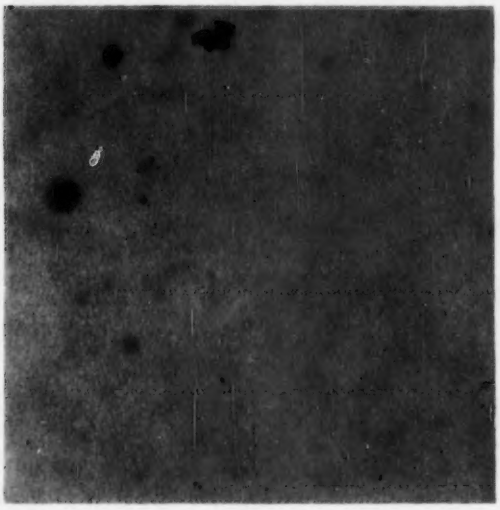

Fig. 5. Ultrathin viscose film dyed with Direct Blue R.

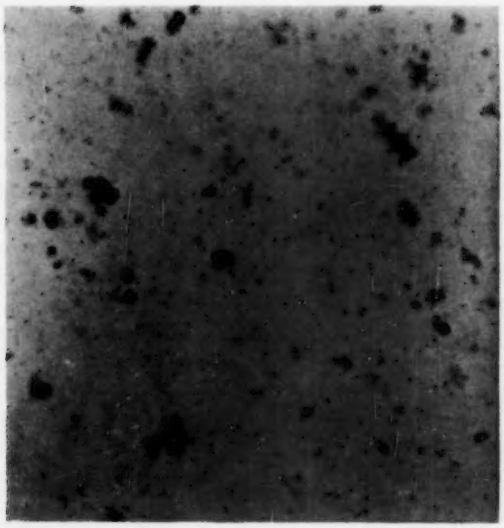

Fig. 6. Ultrathin viscose film dyed with Direct Yellow RL.

For these reasons, a direct correlation between the apparent extent of aggregation of the dyes in the films and their lightfastness on rayon cannot be made. However, it is notable that Direct Blue R and Direct Sky Blue FF, which exhibit very poor lightfastness on rayon (see Table I), are the only dyes examined that do not appear to aggregate in viscose. The other dyes, having considerably better lightfastness on rayon, all aggregate sufficiently in viscose to be detectable with the aid of the electron microscope.

Direct Blue R and Direct Sky Blue FF can be metallized, i.e., can be complexed with a metal such as copper, and Direct Blue RM and Direct Sky Blue FFM are metallized counterparts of those dyes. Both Direct Blue RM and Direct Sky Blue FFM have considerably better lightfastness on rayon than the corresponding unmetallized dyes. Direct Violet RM, another metallized dye, also exhibits good lightfastness on rayon. While the metallized dyes may have enhanced photochemical stability by virtue of the modified electron configuration and resonance of their molecules [4], Figures 2, 4, and 7 are evidence that these dyes tend to aggregate in viscose. It might be inferred from this evidence that the aggregated state of the metallized dyes also contributes to their good lightfastness on rayon.

The results of this study indicate that many direct dyes exist at least partly in an aggregated state in viscose. They also support the idea that the physical

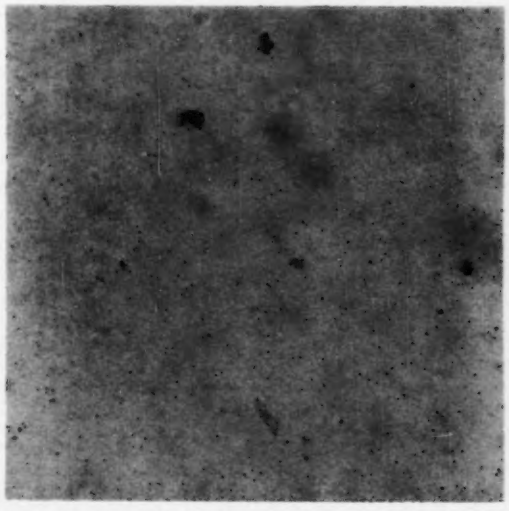

Fig. 7. Ultrathin viscose film dyed with Direct Sky Blue FFM.

state of direct dyes in viscose is important in determining their lightfastness on this material. Additional dyes must be examined before one can conclude whether or not it is the most important factor.

Acknowledgments

The viscose dope used to produce the ultrathin films for this study was generously supplied by Mr. Frederick Morehead, of the American Viscose Corporation. The painstaking efforts of Mr. Martin Botty, of the Stamford Research Laboratories of American Cyanamid, in taking some of the electron micrographs used in this study are gratefully acknowledged.

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Abstract

Investigation of the Factors Affecting the Drapeability of Fabrics[1]

Chauncey C. Chu, Milton M. Platt, and Walter J. Hamburger

Fabric Research Laboratories, Inc., 1000 Providence Highway, Dedham, Massachusetts

THIS research involved a multiplicity of investigations relating to the drape of fabrics. These investigations included (a) a subjective evaluation of drape correlated with Drapemeter (an instrument capable of measuring the projected area beneath a circular fabric specimen which has been draped over a circular support) measurements [1]; (b) interpretation of some aspects of the mechanism of draped samples by references to classical theories of mechanics, principally the flat-plate theory of deformation; (c) evaluation of experimental drape data under a variety of test conditions; (d) examination of the geometry of draped fabrics; (e) discussion of factors influencing the stiffness of fabrics; and (f) measurements of the drapeability of cotton fabrics and of a series of fabrics, with systematically varied geometric parameters, produced from cellulose acetate yarns. Some preliminary conclusions are presented concerning the effects of fiber, yarn, fabric geometry, and finishing on fabric drapeability.

The subjective evaluation of the drapeability of ten selected fabrics (dress goods, suitings, upholstery, and drapery) was performed by 57 respondents who represented a spectrum of backgrounds from housewives to textile college professors. The resultant correlation coefficient of 0.778 between the ranking of the subjective evaluation and the drape coefficient (index of drapeability calculated from data obtained from the Drapemeter; higher values depict poorer drapeability) was considered excellent validation of the FRL Drapemeter.

A reasonably good correlation was also observed between the monoplanar bending characteristics (strip bending length) measured by Peirce's Strip Bending Tester and the multiplanar bending evaluated by the Drapemeter for those fabrics approxi-

[1] *Editor's note:* The research which this abstract summarizes was conducted by Fabric Research Laboratories under contract with the United States Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract was supervised by the Southern Utilization Research and Development Division of the Agricultural Research Service. This abstract is being published in the JOURNAL to call its readers' attention to this study, the detailed final report of which is available from the USDA as an ARS report, Series 72, Number 17.

mately square with respect to stiffness. However, the Strip Bending Tester cannot assess the influence of trellising and buckling of draped specimens and would therefore classify papers and fabrics as equivalent in drape whenever the stiffness in corresponding directions are equal, whereas their draping qualities as given by the drape coefficient and by subjective classification are significantly different.

While this research was essentially an experimental study, it did include analyses of the effects of variations in test conditions on drape. It was demonstrated that the drape coefficient varies with sample size as well as the diameter of the support, but the resulting data were readily converted to the standard conditions for comparison and evaluation.

One of the most important aspects in the understanding of the mechanism of drape was the study of drape geometry, i.e., the configuration of the draped sample. The drape diagram, a projected two-dimensional simplification of the three-dimensional draped sample, contains three items of significance: the area, the number of nodes, and the shape of the nodes. The area is the basis of the drape coefficient (% F). The nodes or pleats are formed in a draped sample by virtue of the buckling of the material. The phenomenon of buckling is related to the elastic properties of the material, the type of load application, and the boundary conditions. It was observed that the number of nodes within any particular sample correlated directly with the drape coefficient for a given test condition. As the test conditions were varied this correlation was no longer evident. However, it was apparent that for any ratio of specimen to support diameters there was a narrow range as to the number of nodes. Assuming that the nodes in a drape diagram are uniform, the drape diagram becomes a cyclic function in polar coordinates. Transferring the polar into rectangular coordinates simplified the analysis of the relationship between the shape factor (ratio of amplitude to wave length) and the drape coefficient. Agreement between calculated and experimental shape factors, for such nodal configurations as semi-ellipses, for example, was found to be excellent, indicating this aspect of drape geometry to be easily predictable from the drape coefficient.

Despite the limited samples available for determining the effect on drape of variations in yarn and fabric geometry, it was evident that the acetate and cotton fabrics responded similarly to structural changes. Weaves with longer floats, reduced cover factors, and decreased yarn diameters resulted in improved fabric drapeability. Yarn twist and fiber cross-sectional morphology were also seen to be influential factors in determining the draping characteristics of a fabric.

In general, it was found that drapeability is dependent on three basic parameters: Young's Modulus, E; the cross-sectional moment of inertia, I; and the weight, W. These factors play important roles in fiber, yarn, and fabric forms. The effect of these quantities on drapeability was expressed as follows:

$$\text{Drape coefficient} = f\,(EI/W)$$

where the function f can involve interactions in these parameters between the warp and filling systems.

The success of the Drapemeter, and the encouraging results of the preliminary investigation of the effect on drape of variations in geometric parameters led to an additional investigation aimed at improving the draping properties of cotton fabrics by varying yarn and fabric structures and application of selected finishing agents.

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Letters to the Editor

Rot-Resistant Finishes for Cotton

Ciba Limited
Basle, Switzerland
August 21, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Berard, Gautreaux, and Reeves [1] of the Southern Regional Research Laboratory, New Orleans, La., published in a recent issue of TEXTILE RESEARCH JOURNAL an article entitled "Formic Acid Colloids of Methylolmelamine as a Weather and Rot-Resistant Finish for Cotton." The authors claim that their method gives rot resistance of better durability than conventional procedures. They also claim their method to be superior to the Arigal [1] process because of the shorter fixation time needed and because only conventional equipment is required for their process.

They have clearly demonstrated that their method gives a more durable rot resistance than other methods based on impregnation with resin followed by drying and curing.

A better durability of the preservation effect is certainly an advantage over previous dry curing resin application methods. However, the claim of superiority over the Arigal process is not justified and prompts us to comment on the authors' paper.

Before making any comparisons we would like to discuss the development of resin application in acid solution, as a background for both the authors' method and the Arigal procedure in its present form. As long ago as 1945 Ciba recommended a "Formic Acid Method" to impart resistance to swelling and wet strength to rayon with Lyofix A,[1] a melamine formaldehyde condensation product. In the Ciba circular describing the above process [2], special attention was drawn to the instability of the solution, which resulted in a harsher handle when the goods were treated in long-standing baths. For fixation, the impregnated textiles were dried and cured in the usual manner. Swelling and wet strength being no problem with natural cellulosic fibers, a similar treatment was not recommended for cotton. Tests on cotton, carried out in Ciba laboratories using melamine formaldehyde condensation products dissolved in formic acid, were discussed by Dr. Landolt in 1947 [4].

He mentioned that the solutions used for the treatment contained positively charged particles. Furthermore, Dr. Landolt commented on the improvement in weatherfastness of textiles so treated. The improvement of rot resistance by melamine formaldehyde condensation products was already known at that time [6]. However, despite the fact that more than ten years ago it was known that the rot and weather resistance of natural cellulosic fibers could be improved by a treatment with solutions of melamine formaldehyde condensation products—and this with the conventional method as well as with the formic acid method—this treatment was rarely used on a practical basis as a rot-resistant finish. The main reason for this reluctance was not lack of durability of the rot resistance but the reduction in strength of the natural cellulosic fiber which takes place when treated with thermosetting resins by the conventional process.

Early work by Ciba aimed at producing good rot resistance with a minimum loss in fiber strength by careful control of the conventional dry curing method. This approach was not successful. The use of acid colloids, based on a Ciba formula for the production of wet strength paper, was also tried. This method involved the use of aged hydrochloric acid solutions of the melamine resin Ciba 286. Trials with this process showed that freshly prepared solutions of melamine resin in acid gave a good preservative effect. However, solutions aged to the stage of acid colloids with substantive properties gave only poor performance. The best results were obtained by treating the fabric with an unaged or only slightly aged solution of melamine resin in formic acid and leaving the fabric to stand in the wet state to allow condensation of the resin to proceed. In contrast to the normal method of fixation by drying and curing, this method did not result in fiber strength loss.

Based on the above findings, patent applications for the Arigal process were filed by Ciba in 1952. The process is now protected in many countries; see e.g. [3].

[1] Registered trademark of Ciba.

In these patents, it was stated that when using solutions of aminoplasts to which acids had been added these solutions should be fresh because during standing changes might take place in the solutions which would decrease their suitability for the purposes intended by the invention. Example No. 1 in the patent suggests the use of a trimethylol melamine formic acid solution.

Since then many practical improvements have been made. Completely stable, slightly alkaline, aqueous solutions of Arigal C containing Catalyzer C are now used instead of formic acid baths, which in higher concentration change rather quickly. More rapid fixation is achieved by temperatures of about 100° C., or even higher when under pressure, by use of direct steam. Patent applications have been filed for these improvements. One point remains strictly unchanged: the principle of wet fixation in order to fully maintain the mechanical properties of the fiber. Even though wet fixation requires more time than dry curing, the practical feasibility of large scale production by suitable adaption of processing conditions and existing equipment has been demonstrated in European plants. We are confident that in the U. S. as well, there will be a similar development.

The method recommended by Berard, Gautreaux, and Reeves has the very grave disadvantage of fiber damage against which the advantage of shorter fixation time seems a rather small gain, even though it may allow the use of equipment commonly found in the United States.

This advantage in application is, however, more than offset by disadvantages also pertaining to application. Instead of being able to work with nearly neutral solutions as recommended for the Arigal process, one is compelled to use solutions containing 200 g. formic acid per liter. Thus, after curing, a rinse and subsequent additional drying will be necessary, whereas the Arigal process requires only one drying with or without a previous rinse.

A serious additional factor is the instability of the impregnating solution. The article mentions an 8-hr. stability. However, the authors' findings indicate that baths which had been standing for only 2 hr. had already lost some of their preservative effect as compared with fresh baths. Thus, even 2 hr. is too long a time. On the other hand, Arigal baths have been used under plant conditions for a week and at the end of this time were still satisfactory.

From the figures given in the article it appears to be necessary to have a resin content of at least 12% for best results. With less resin the results after 15 weeks soil burial were not entirely satisfactory. No strength decrease whatsoever was detected in a cotton material containing only 10% Arigal after 24 weeks soil burial at 30° C., whereas samples of acetylated and cyanoethylated cotton subjected to the same test were destroyed [5]. The even distribution of resin achieved with the Arigal process is certainly an advantage over the "controlled penetration" obtained by the authors' method. Both the Arigal process and the method suggested depend for their effect on a physical barrier to microbial attack. It is surely better that the barrier extends throughout the fiber where it cannot be rendered ineffective by abrasion. The authors experimented on a print cloth. On a fabric of such light weight it is unlikely that difficulties would be experienced in wetting out the fabric evenly. On the other hand, heavier fabrics are more difficult to wet out. The thorough wetting of such heavy weight fabrics is assisted in the Arigal process by the fixation procedure, during which the fabric is maintained in a warm wet condition.

We have a high respect for the work of the Southern Regional Research Laboratory, New Orleans, La., in the field of rotproofing of cotton and we agree with them that protection by resin application offers the best hope for success.

However, in our opinion, methods based on dry curing should be considered only when rot resistance is not the primary aim of the treatment. When crease resistance or wash and wear properties are the desired effect, a certain loss in fiber strength is acceptable. This is not the case where rot resistance must be obtained. The Arigal process gives very good protection without the usual loss in strength and is, therefore, in our opinion, still the best answer to the problem of rot-resistant cotton.

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ANDREAS RUPERTI

Reply to Ruperti Letter

Southern Regional Research Laboratory[1]
New Orleans, Louisiana
September 11, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The paper "Formic Acid Colloid of Methylolmelamine as a Weather and Rot Resistant Finish for Cotton" was intended merely to present a practical method for producing cotton fabric with outstanding rot resistance and improved weather resistance. The paper was not intended to claim that the process or finish was superior to all other finishes or to imply that this was the first use of an acid colloid of methylolmelamine. Our paper stated "cotton fabric finished with the acid colloids compares favorably with partially acetylated, fully acetylated, cyanoethylated, and Arigal fabrics which are known to have excellent resistance to rot." Several references were cited to show that others had found that methylolmelamine type resins improve rot and weather resistance of cotton; the application of acid colloids for various purposes was also cited. The work of Dr. Landolt, referred to in Dr. Ruperti's letter, did not mention rot resistance and his reference to weathering was concerned with improving the lightfastness of vat dyes when exposed to light and weathering.

Our published work showed that the finishing of print cloth by the acid colloid technique reduced the original strength of the fabric by about 20–25%. In unpublished work, the strength loss of an Arigal finished print cloth (finished by Ciba, Limited of Switzerland) was 6–7%. Therefore, the Arigal finished fabric is slightly stronger initially, as stated by Dr. Ruperti.

As to the advantage of one process over the other, this might be determined by the facilities available at a particular finishing plant. We had merely stated that a steam cure process requiring about an hour or longer, as in the Arigal process, is inconvenient for many American finishing plants. Perhaps a brief description of the processes, as published, for application of the acid colloid finish and of the Arigal finish would allow a comparison of the two processes.

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

Application of the acid colloid finish. Seventeen parts of a commercially available methylolmelamine is dissolved in 63 parts of water and then 20 parts of formic acid is added. Fabric is padded through the solution, dried, and cured in the usual manner of resin finishing using conventional textile processing equipment. The fabric is then washed and dried.

We have recently been advised by a commercial finisher that for continuous operation with the colloid finish the two liquids—water solution of methylolmelamine and formic acid—can be added to the pad trough simultaneously and continuously at the proper rate and thus maintain fresh solution at all times.

Application of the Arigal finish. (See Example 1 of U. S. Patent 2,763,574 as referred to by Dr. Ruperti in the above letter.) ". . . Cotton twist . . . is immersed in a freshly prepared solution containing 60 gm. of condensation product of limited water-solubility from 1 mol of melamine and 3 mol of formaldehyde, 24 gm. of formic acid, 1 gm. of nonionogenic wetting agent per liter, at room temperature, turned several times in the bath and compressed in order to expel the air contained in the yarn, hydroextracted to 170 percent of the original yarn weight and stored for a long time (overnight or for 1–3 days) in a closed vessel. It is thereupon rinsed, first with dilute ammonia solution and then very thoroughly with water and dried."

According to Example 4 of the same patent, cotton fabric can be treated on the foulard, then squeezed off to 190% of the original weight and cured in a hot steam chamber. The curing operation alone required about 45 min. According to Dr. Ruperti's letter, improved processes have been discovered by Ciba and these (apparently unpublished) still require the "principle of wet fixation."

Dr. Ruperti stated that both the Arigal and the acid colloid finishes depend upon a physical barrier for their resistance to microbial attack. This may be true of Arigal-finished fabric, in which there is apparently little reaction with or cross-linking of the cellulose. However, there is more extensive cross-linking in acid colloid-finished cotton fabric, and this too undoubtedly affects the rot resistance of cotton.

With respect to penetration of heavy fabrics by the acid colloid finish, current research (to be published soon) has demonstrated that the acid colloid

is effective in imparting rot and weather resistance to drill and duck fabrics.

In summary, we have pointed out that the acid colloid finish for cotton fabrics is a practical method for producing fabrics with outstanding rot resistance and good weather resistance. The finish reduces the initial strength of the fabric by about 20–25%, but it is applied using commercially available chemicals and conventional textile finishing equipment. It should be a relatively inexpensive method of producing fabrics with durable rot and weather resistance.

W. NORBERT BERARD
GLORIA A. GAUTREAUX
WILSON A. REEVES

Effect of Acetyl Groups on the Strength of Jute Fiber

Technological Research Laboratories
Indian Central Jute Committee
Regent Park, Calcutta 40
India

September 15, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The presence of acetyl groups in jute fiber was shown [2] and the occurrence of an ester linkage between the carboxyl group of uronic acid and the hydroxyl group of lignin in jute was suggested [3] by Sarkar many years ago. Recently, Klauditz [1] has shown that 0.2% NaOH at 20° removed most of the acetyl groups from birch or aspenwood and the tensile strength fell by about 50–60%. The decrease in strength is ascribed to the rupture of the bond between lignin and hemicellulose. It was, therefore, considered worthwhile to see if jute fiber behaved likewise. Acetyl groups are almost completely removed from jute by 1% NaOH in the cold. Representative samples, two *capsularis* and two *olitorius*, were extracted with alcohol-benzene. Standard fiber bundles, in pairs, were made from these and the ends of each tied up for strength tests. One of each pair was treated with 1% NaOH (fiber : liquor ratio 1 : 50) at ordinary temperature for 2 hr., washed with water, then with dilute acetic acid, and finally with water; these were dried in air. Acetyl value was determined for each; the results are shown in Table I. The fiber bundles (20 mg./in., 10 in. long) were broken on a pendulum-type tensile strength tester; the results are given in Table II. The controls were treated with distilled water in the same manner as with alkali. It will be seen that, in the case of jute fiber, the tensile strength is not significantly affected by the breaking of ester linkage between lignin and uronic acid.

TABLE I

Sample	Acetyl value* Before alkali treatment	Acetyl value* After alkali treatment	Loss in wt. on alkali treatment, %
J–4575 (O)	75.40	0.78	4.56
J–5565 (O)	72.52	0.78	5.92
J–5462 (C)	85.90	0.50	6.22
J–5286 (C)	90.04	0.56	7.81

* Milliequivalents per 100 g. of oven-dry jute.

O—*olitorius;* C—*capsularis.*

TABLE II

Sample	Strength (breaking length in km.)* Treated with water	Strength (breaking length in km.)* Treated with NaOH	Difference	Student's *t*
J–4575 (O)	15.8 ± 0.46	14.2 ± 0.47	1.6	2.43
J–5565 (O)	19.2 ± 0.45	20.0 ± 0.37	−0.8	1.30
J–5462 (C)	20.8 ± 0.67	19.7 ± 0.55	1.1	1.26
J–5286 (C)	12.2 ± 0.55	11.7 ± 0.49	0.5	0.64

* Mean of 50 observations in each case. The value of *t* for 98 degrees of freedom (1% level of significance) is 2.63.

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P. B. SARKAR
A. K. MAZUMDAR
S. B. BANDYOPADHYAY

Studies in the Reaction of Formaldehyde with Cellulose

Department of Chemical Technology
University of Bombay
Matunga, Bombay 19
India

September 21, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Aqueous formaldehyde does not combine with cellulose to an appreciable extent in presence of an acid catalyst if water is not progressively removed from the system [6, 7]. The general practice is to remove the water by subjecting the material containing formaldehyde to drying and baking treatments. This involves keeping the material at an elevated temperature, which results in a continuous change in the concentration of formaldehyde and the catalyst present on the fiber. Hence, the actual conditions under which the reaction takes place are not known [6, 12]. Methods using nonaqueous media are either drastic [13] or give poor formaldehyde uptake [3].

Whinfield [11] has reported that the reaction between aqueous formaldehyde and cellulose can be carried out at room temperature if the cellulose is treated with acidified formaldehyde solution containing a large amount of a hygroscopic salt. As this method does not involve any drying or heating operation, it is possible to determine accurately the actual concentration of various ingredients throughout the course of the reaction. It is also possible to carry out this reaction satisfactorily with heat-sensitive modified celluloses. The present investigation was undertaken to study the behavior of cellulose towards formaldehyde under various conditions of treatment and to elucidate the kinetics of reaction between cellulose and formaldehyde. Calcium chloride was used as the hygroscopic substance and was added to acidified formaldehyde reaction mixture. Various cellulosic fibers were treated at different temperatures (15–60° C.) with aqueous formaldehyde solutions (25–125 g./l. formaldehyde) containing different amounts of hydrogen chloride (10–40 g./l.) and appreciable amounts of calcium chloride (250–600 g./l.) for different periods up to 96 hr. The amount of chemically combined formaldehyde, after washing the samples free of adsorbed formaldehyde and conditioning, was determined colorimetrically [1]. A study of kinetics of the reaction under these conditions at different temperatures indicates that the reaction is of the first order with respect to formaldehyde concentration in the bath. In most cases at $30 \pm 1°$ C. an equilibrium was established within a period of 24 hr. when the amount of combined formaldehyde increased linearly with the concentration of formaldehyde in the bath. The concentration of formaldehyde combined with the fiber substance at equilibrium (calculated on the basis of effective volume of cellulose, assuming moisture absorption values as determined by various workers [5, 8, 9] hold good for different fiber substances under investigation) and that in the solution, approach nearly the same values when the amount of calcium chloride present in the reaction mixture is 500 g./l. The acid concentration in the reaction mixture did not appear to have much effect on the reaction. The amount of combined formaldehyde increased to a maximum with an increase in the concentration of calcium chloride up to 500 g./l. and subsequently showed a reduction. The amount of combined formaldehyde also decreased with an increase in the crystallinity of a fiber substance, and vice versa. Rates of reaction calculated in the case of standard cellulose are given in Table I. The apparent energy of activation for the reaction calculated from the rates of reaction in the initial stages at different temperatures was found to be of the order of 5.6 kcal./mole.

The investigation was further extended to oxycellulose and hydrocellulose samples which were also treated with chlorous acid [2] and sodium borohydride [4]. The results indicate that carboxyl groups play an important role in determining the amount of formaldehyde combining with the material. It is felt that such a study may help to explain the mechanism of oxidation of cellulose by various oxidizing agents.

TABLE I. Initial Rates of Reaction of Formaldehyde with Cellulose

Temperature, ° C.	Calculated rate constants, sec.$^{-1}$
18.0	10.0×10^{-5}
33.0	17.8×10^{-5}
42.5	25.3×10^{-5}

The study also includes the comparison of the reaction of formaldehyde with cellulose with that of a reactive dye which is known to react with cellulose under alkaline conditions [10]. Cellulose and modified celluloses were dyed with reactive dyes. Dyed samples were treated with formaldehyde, and undyed samples after being treated with formaldehyde were dyed. A study of the physical and chemical properties of the dyed and undyed methylene celluloses is in progress. The detailed results will be published elsewhere.

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K. V. DATYE
G. M. NABAR

Applicability of the Alkaline Thioglycollate Extraction Test for Detection of Wool Damage[1]

Forschungsinstitut der Hutindustrie e.V.
Mönchengladbach, Germany
August 17, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

It is known from literature that the determinations of alkali solubility by the method of Harris [2] and of acid solubility by the method of Zahn [4] or Fröhlich [1] are means of detecting damage in wool products and animal hairs. A short time ago in your journal a new method for detecting damage in wool, the "alkaline thioglycollate extraction test," was described by Lennox [3]. In connection with experiments for determination of damage to hare- and rabbit-hairs during carrotting, we included the alkaline thioglycollate extraction test and checked the applicability of this new test on differently treated wools. The results are given in Table I. It shows that the alkaline thioglycollate extraction test responds preferably to acid damage. The solubility of alkali treated wool decreases very much, while the solubility of wool treated with hydrogen peroxide increases only slightly. This shows that the alkaline thioglycollate extraction method of Lennox gives with acid and alkali treated wool results similar to those of the alkali solubility test of Harris. While wool treated with oxidizing agents responds clearly to the alkali solubility test, it shows much less response to the alkaline thioglycollate test (see Table I), so that simultaneous determination of alkali solubility

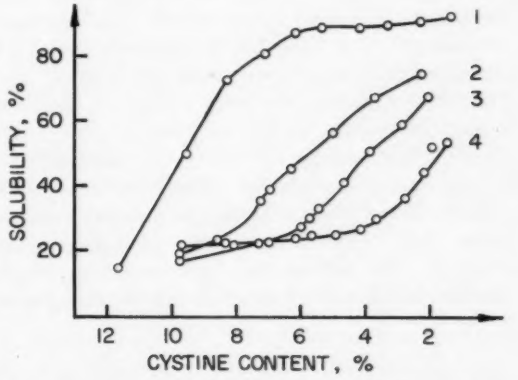

Fig. 1. Relationship between cystine content of wool and alkaline thioglycollate extraction, alkali solubility, and acid solubility. (1) Alkali solubility; (2) acid solubility, 0.8 *N* HCl; (3) acid solubility, 4.5 *N* HCl; (4) alkaline thioglycollate extraction.

[1] Translated by Hedwig Knauer.

TABLE I. Comparison of the Alkaline Thioglycollate Test with Alkali and Acid Solubility

Treatment		Length of treatment, min.	Temp., °C.	Alkaline thioglyc. extraction	Alkali solubility, %	Hydrochloric acid solubility, %			Swelling,* %
						4.5 *N*	0.8 *N*	0.3 *N*	
None				15.9	14.5	6.1	13.1	1.6	46–47
Calc. soda	2% sol.	30	50	2.65	11.2	9.4	15.4	3.5	53.5
		90	50	1.20	8.7	9.9	16.0	3.7	55.1
		180	50	.82	6.6	11.1	16.8	4.0	57.2
		180	65	.00	4.25	12.4	19.4	3.8	60–61
	1% sol.	60	20	—	14.2	8.0	15.1	3.4	49–50
		30	50	6.8	10.3	9.0	13.9	3.5	52.6
		90	50	2.4	8.5	9.2	14.7	3.4	52.8
		180	50	1.5	6.2	9.8	16.2	3.2	53.1
Soda-soap solution									
2 g./l.		30	50	14.2	15.0	8.7	—	—	48.6
5 g./l.		60	50	14.0	14.8	8.6	—	—	48.3
Hydrogen peroxide 35%									
	2% sol.	30	50	18.7	23.4	8.6	15.6	1.8	44.8
		90	50	20.7	30.0	10.7	18.3	3.6	46.0
		180	50	23.0	44.5	13.8	20.8	4.0	47.8
		300	50	25.8	55.2	15.2	24.6	5.4	48.1
Sulfuric acid	0.1 *N*	15	100	27.0	29.4	10.4	16.4	3.9	47.2
		30	100	32.0	35.6	10.6	17.8	5.0	46.8
		90	100	59.3	65.1	11.0	18.0	5.3	49.2
		180	100	89.5	75.1	12.1	19.3	6.2	49.0
	0.02 *N*	90	100	30.0	38.6	11.1	18.4	5.3	48.4
		180	100	40.8	43.4	11.4	20.0	5.6	47.6

* Swelling determined by overnight watering (distilled water) and following centrifuging for 3 min. at 3500 cycles/min.

and alkaline thioglycollate extraction constitutes a means of distinguishing between acid and oxidic damage. In Figure 1 we show the dependence of alkali-, hydrochloric acid-, and thioglycollate solubility upon the cystine contents of the wool specimen (the samples were prepared by treatment with 1.6% peracetic acid, liquor : goods ratio 50 : 1, at 20° C.). The alkali solubility test very sensitively indicates cystine dissociation, as Figure 1 shows, whereas the alkaline thioglycollate extraction test responds only to high cystine dissociation. Therefore this test, in contrast to the alkali solubility test, shows little reaction with wool treated with oxidizing agents (H_2O_2). We believe the high sensitivity of the alkaline thioglycollate extraction test for acid treated wool is due to the preferred response to dissociation of peptide bonds. The acid solubility tests also respond much less than the alkali solubility test to the dissociation of cystine.

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